Energy Applications of Gas-Surface Interactions in Nanoporous Materials

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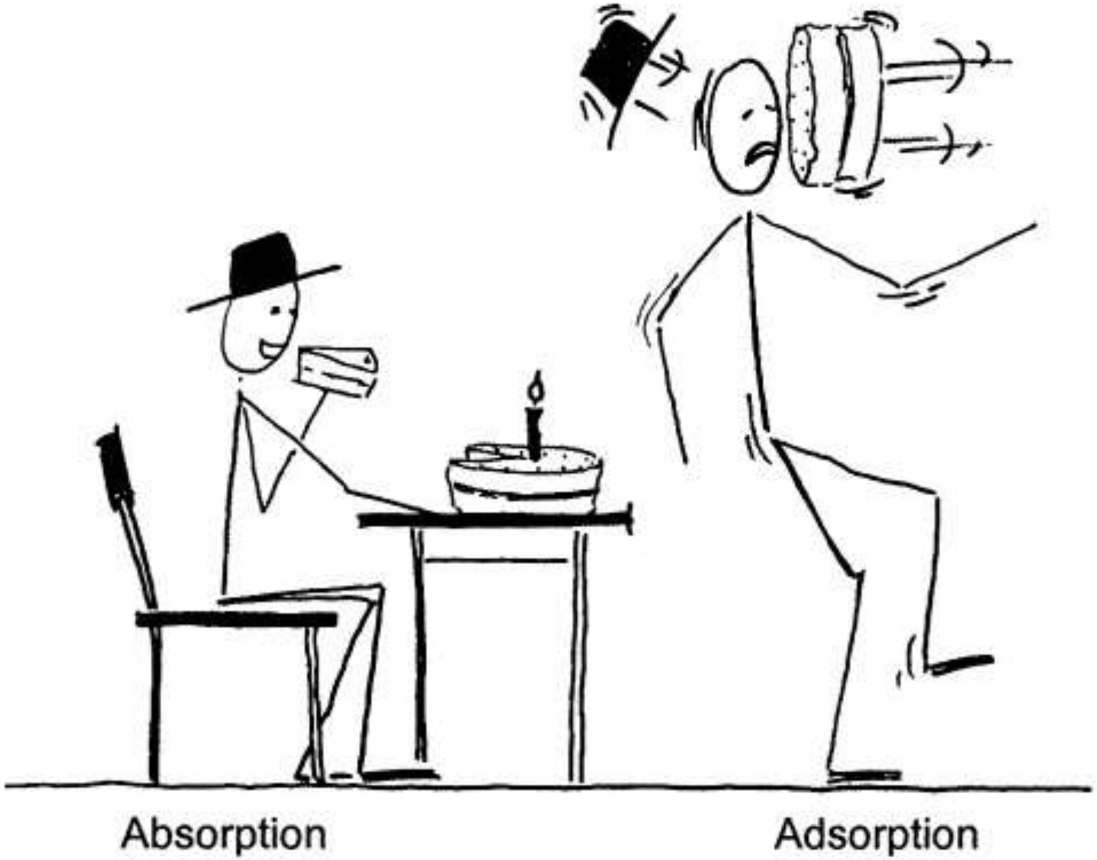
Some Terminology

Absorption v. Adsorption

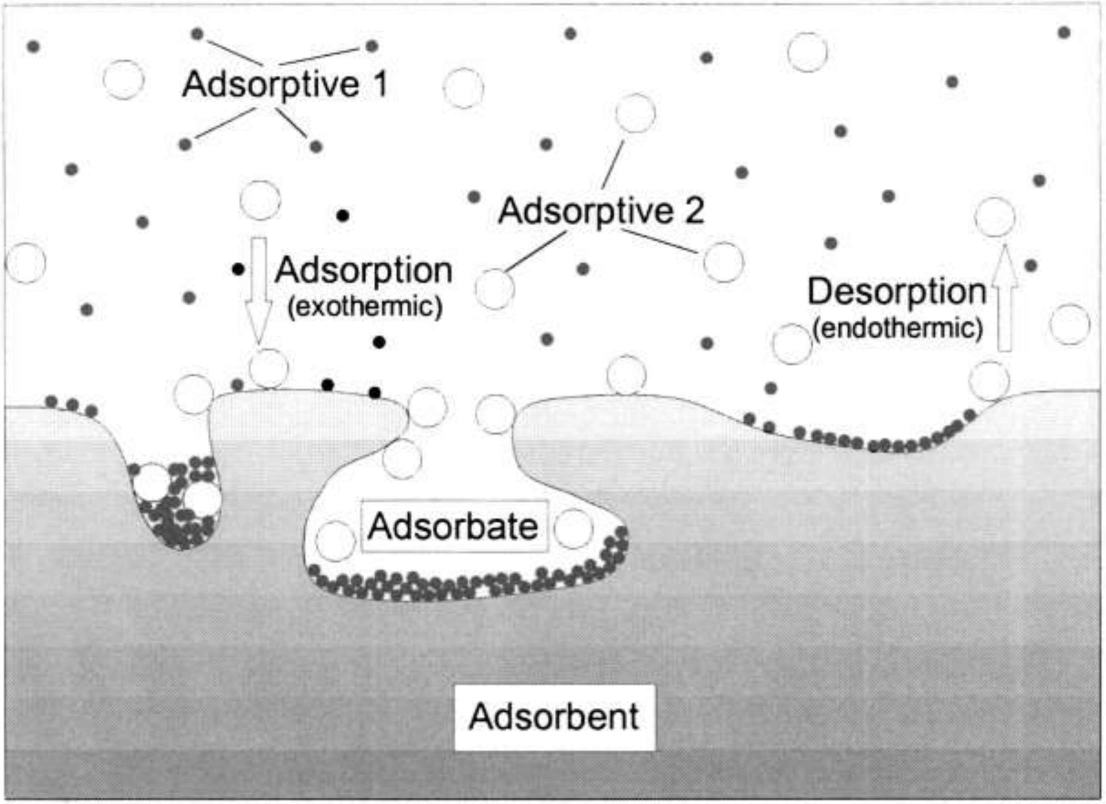


- Face=Solid Material
- Cake=Gas or Liquid
- Sorption: Absorption & Adsorption

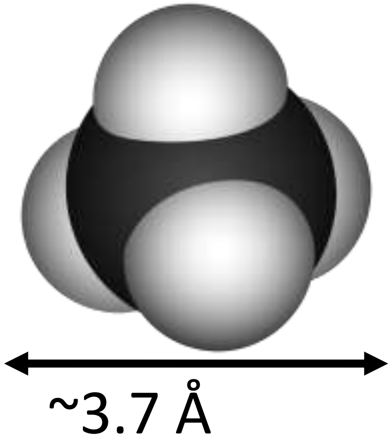
van der Waals

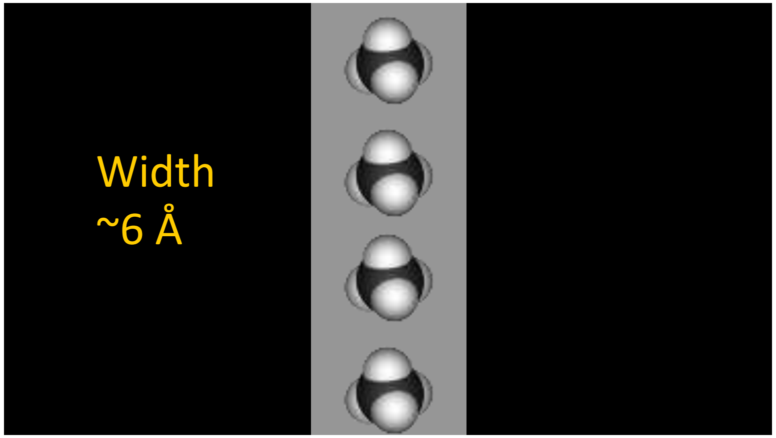
Adsorption

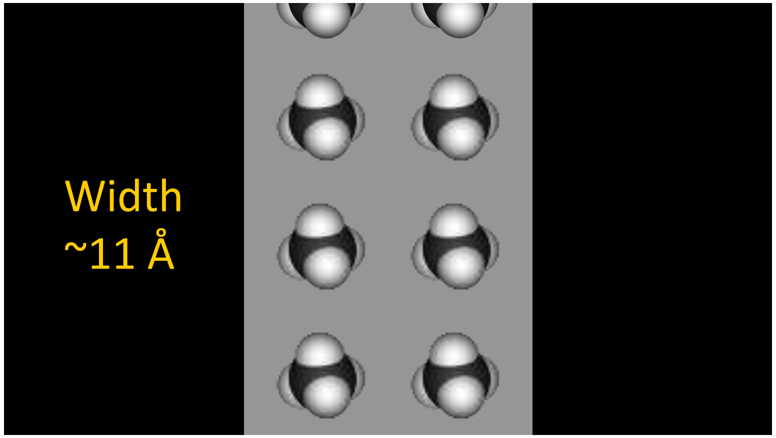
- Adsorptive
  - Gas or liquid
  - Molecules interact with the surface atoms of adsorbent
- Adsorbent
  - Solid
  - External & internal surfaces exposed to adsorptive
- Adsorbate
  - Molecules being adsorbed on the surface
  - Separate phase

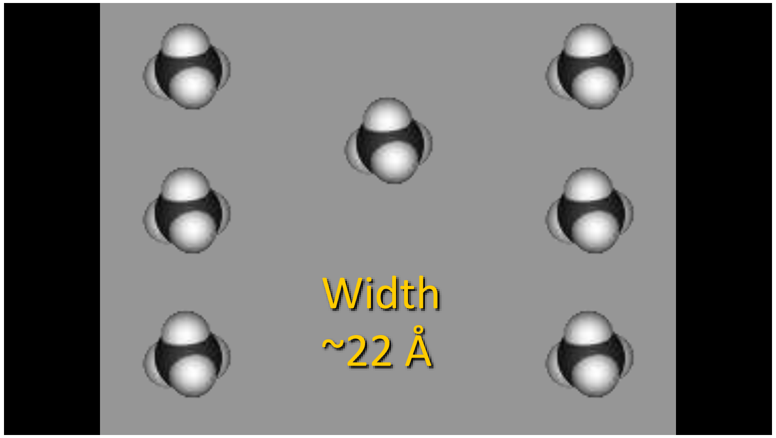


Why are Nanopores Important?



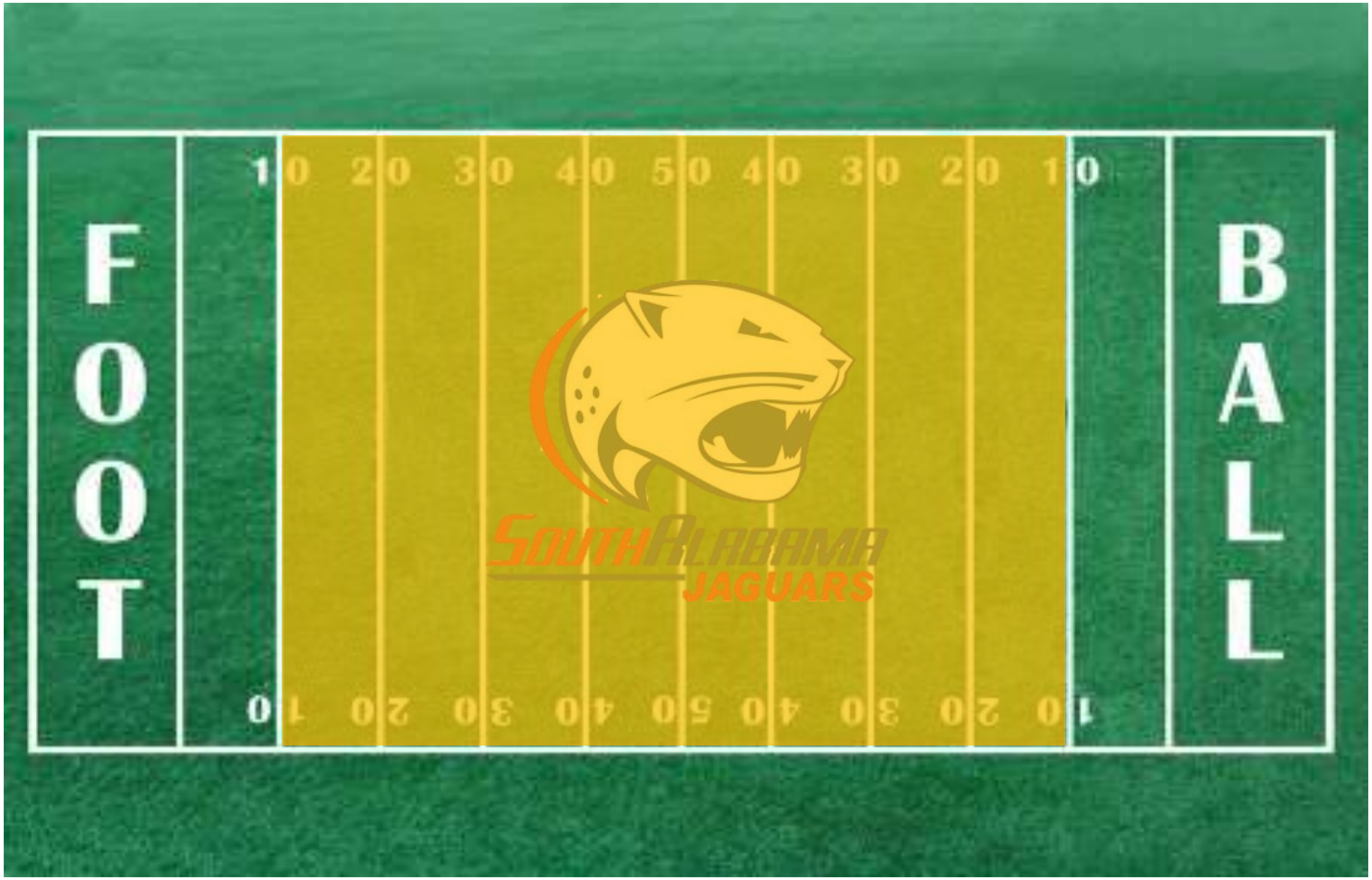




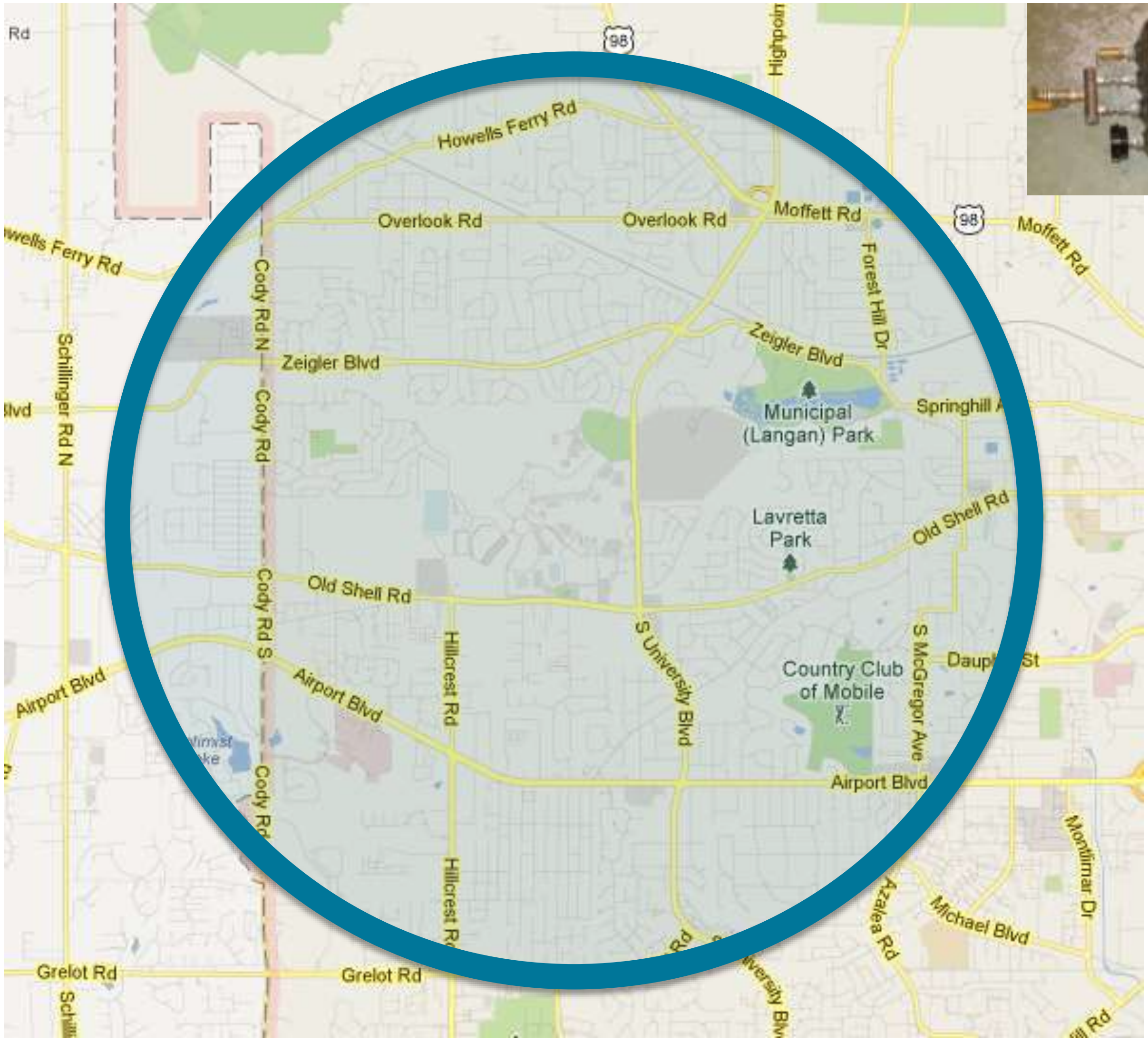


Large Surface Area

These sorbents have up to 3,000 m^2/g



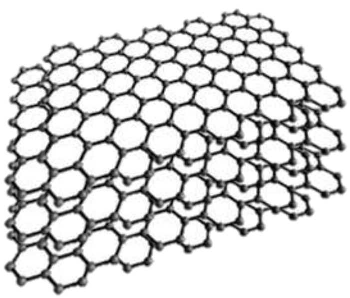
Large Surface Area

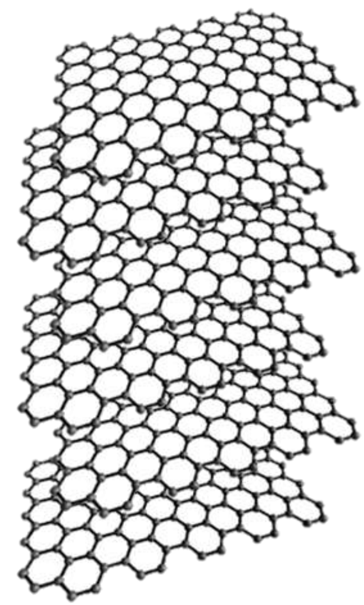


Large Surface Area

5 cm^2/g

30,000,000 cm^2/g

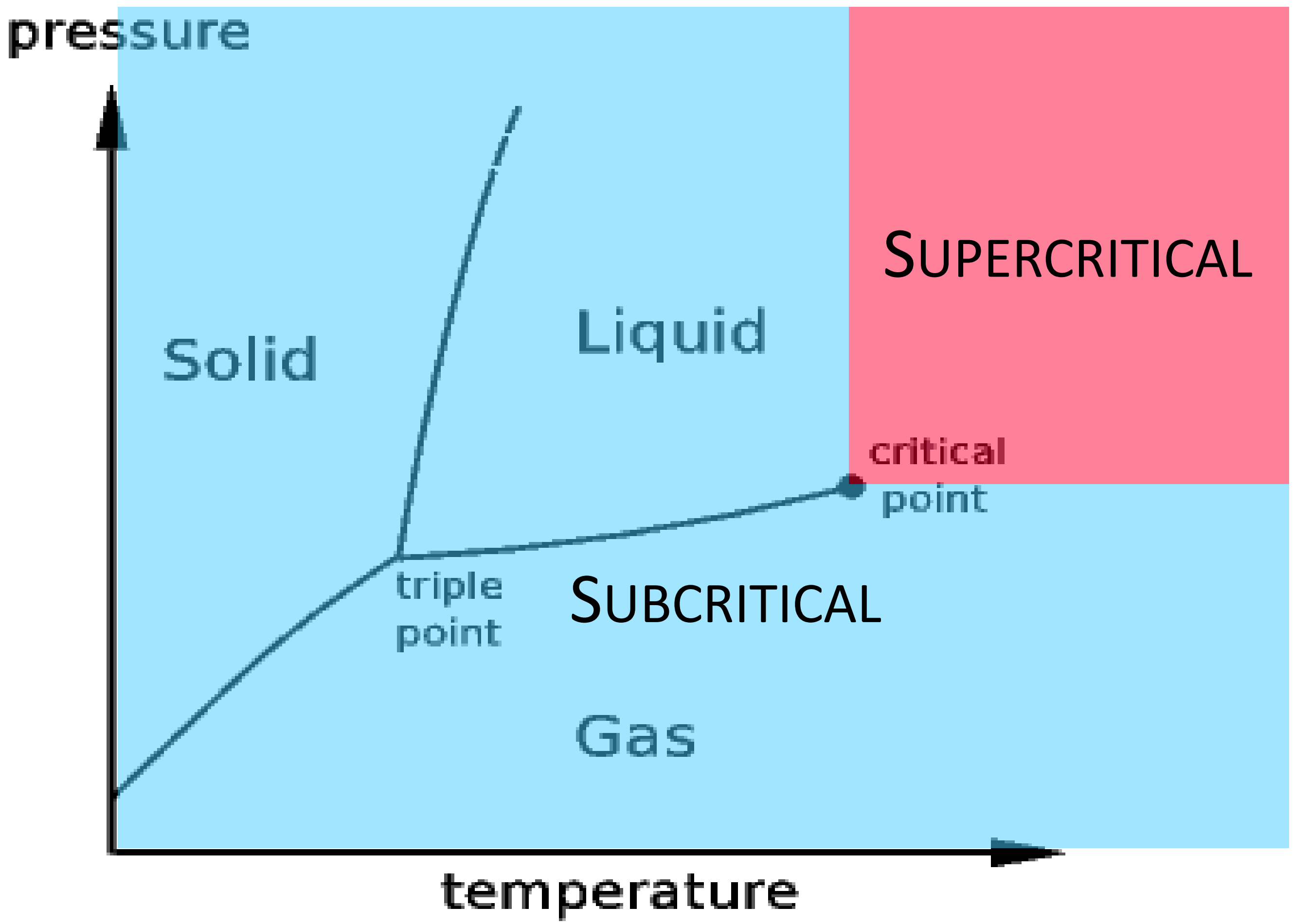




High Porosity

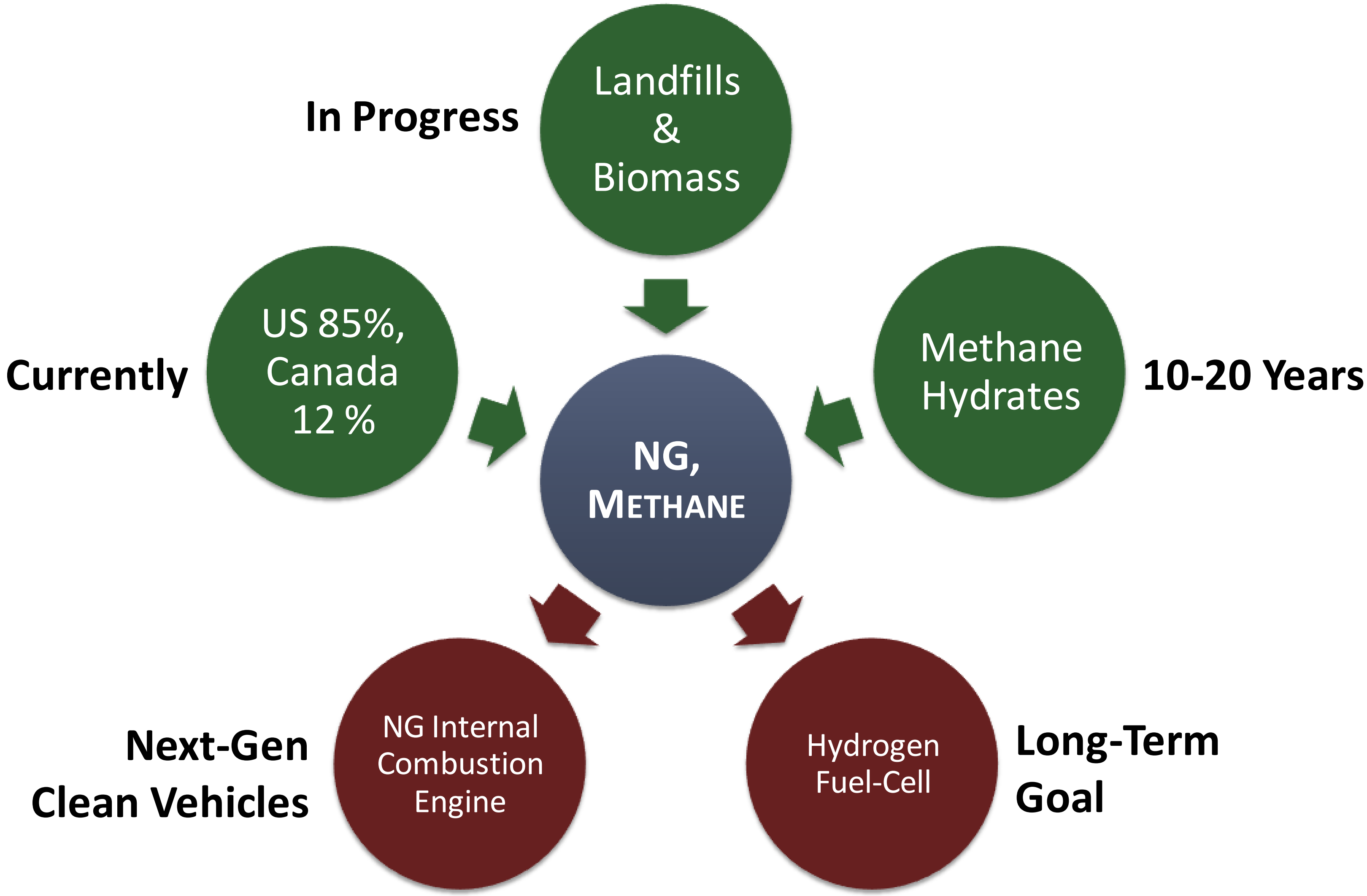
These sorbents have porosities up to 80 %

Thermodynamics



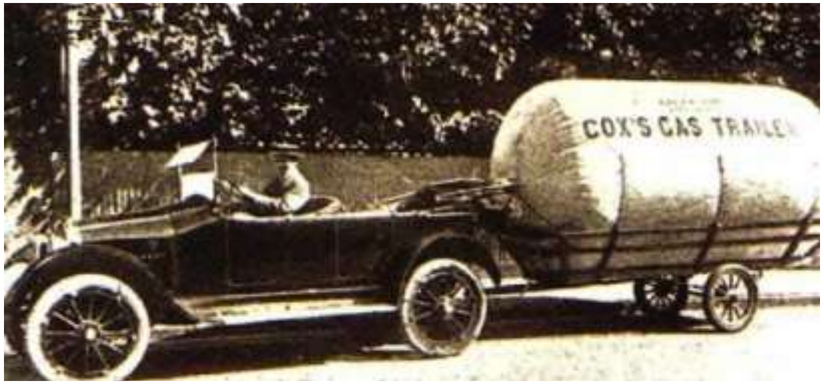
Natural Gas & Hydrogen Storage

Motivation


In Progress
Landfills
&
Biomass
Currently
US 85%,
Canada
12 %
Methane
Hydrates
10-20 Years
NG,
METHANE
Next-Gen
Clean Vehicles
NG Internal
Combustion
Engine
Hydrogen
Fuel-Cell
Long-Term
Goal

Natural Gas Vehicles Over Time

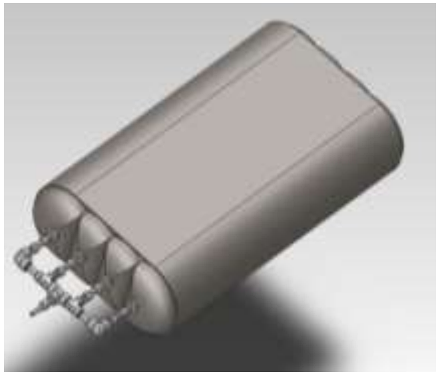
First NG vehicle 1910 (USA) with balloon tank on trailer



NG vehicle ~1930 (France) with balloon tank on roof

Current NG vehicle with high-pressure tank in trunk

Low-pressure, flat-panel ANG tank

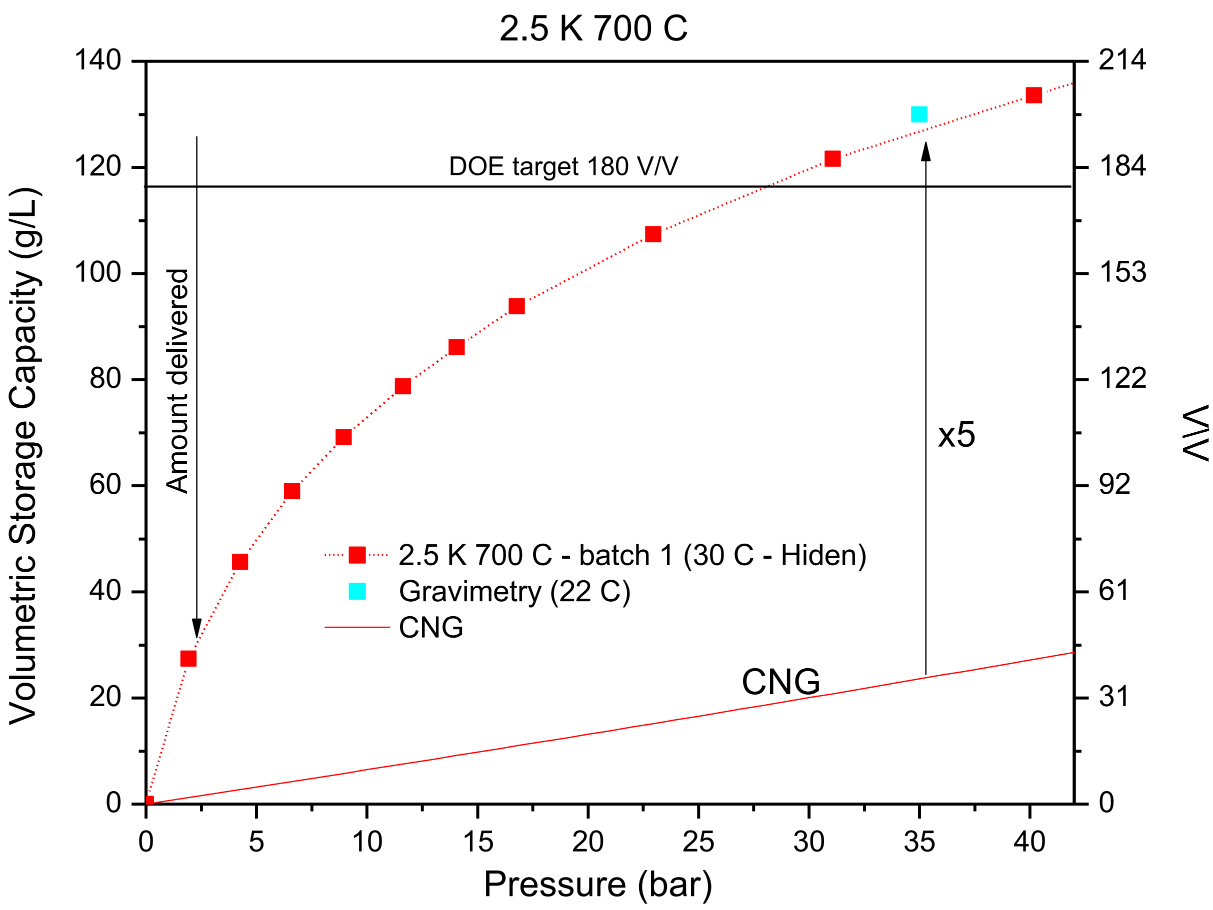


Future NG vehicle with low-pressure tank in unused space


Prototype Tank
Natural gas
methane molecule
Future Tank
Courtesy of the National Science Foundation, by Nicolle Rager Fuller

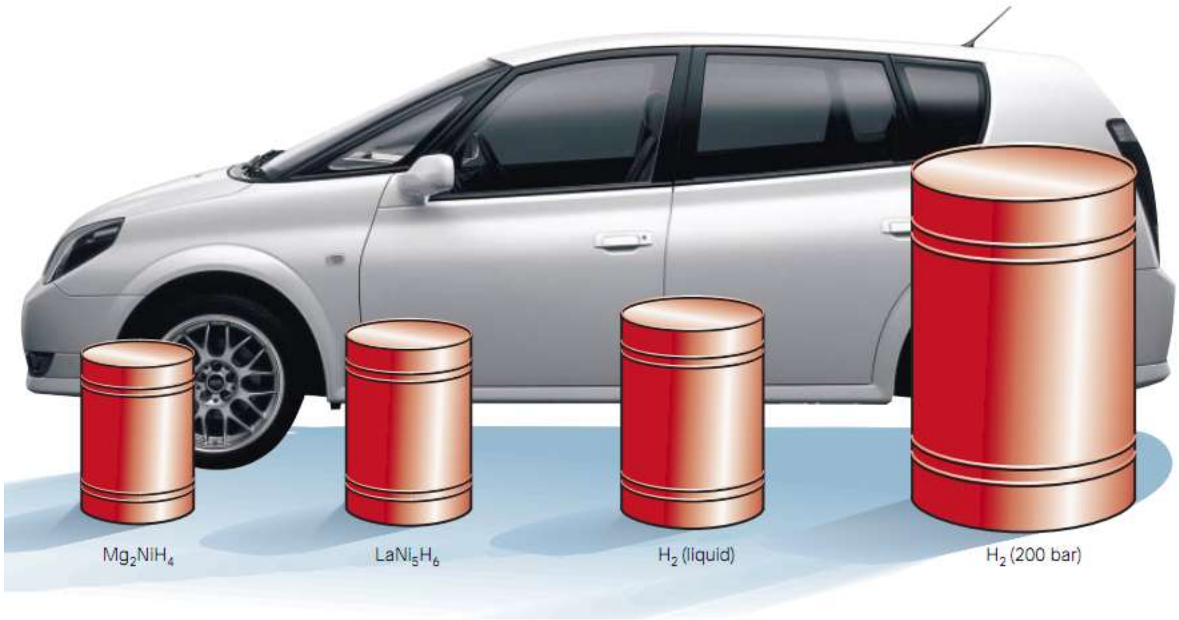
Best Volumetric Storage Capacity of MU Carbon Powder

- Target pressure for flat tank:
  - 35 bar (35 atm, 500 psig)
  - w/out adsorbent: 150 bar
- DOE target capacity:
  - 118 g/l



Hydrogen Storage Systems

Hydrogen occupies a very large volume



Schlapbach & Züttel. *Nature*, **414** (2001) 353-358.

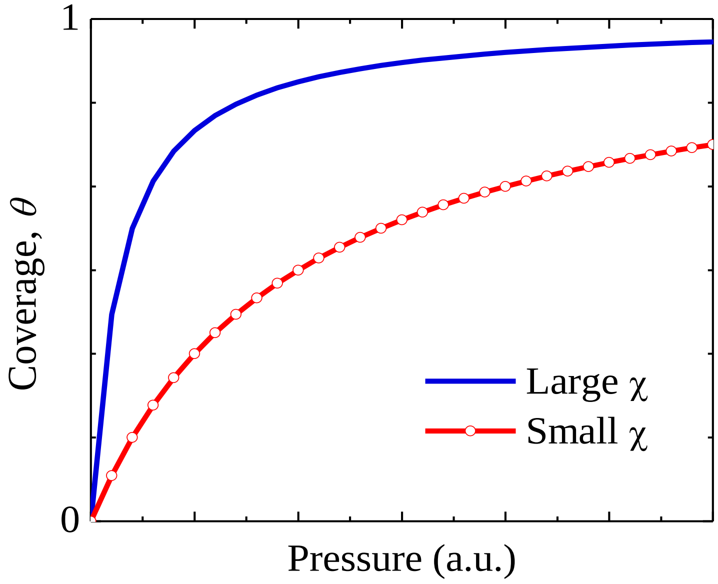
1 kg H_2 ≈ 1 gal. gasoline equivalent

Langmuir Theory of Gas Sorption

1) Fixed number of sites
2) Monolayer adsorption
3) Energetically homogeneous
4) Interactions: adsorbate-surface
   - no adsorbate-adsorbate

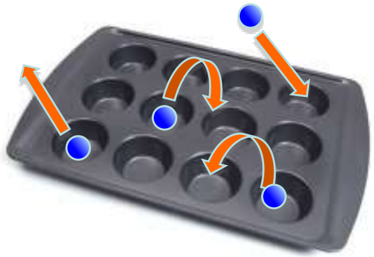
$$\theta(p,T) = \frac{\chi(T)p}{1+\chi(T)p}$$

$$0 \le \theta \le 1$$



Localized or Mobile

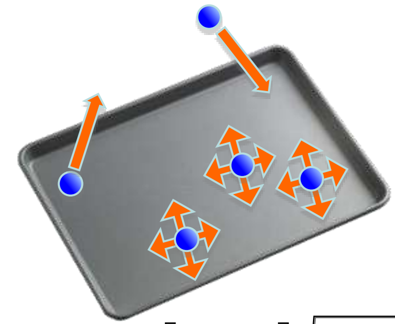
Localized



$$\chi_{Local}(T)=\frac{\exp\left[\frac{E_B}{N_A k_B T}\right]\sqrt{\frac{h^6}{(8\pi M_{Gas})^3 (k_B T)^5}}}{\left[\sinh\left(\frac{h\nu_x}{2k_B T}\right)\sinh\left(\frac{h\nu_y}{2k_B T}\right)\sinh\left(\frac{h\nu_z}{2k_B T}\right)\right]}$$

$$\theta(p,T)=\frac{\chi(T)p}{1+\chi(T)p}$$

Mobile

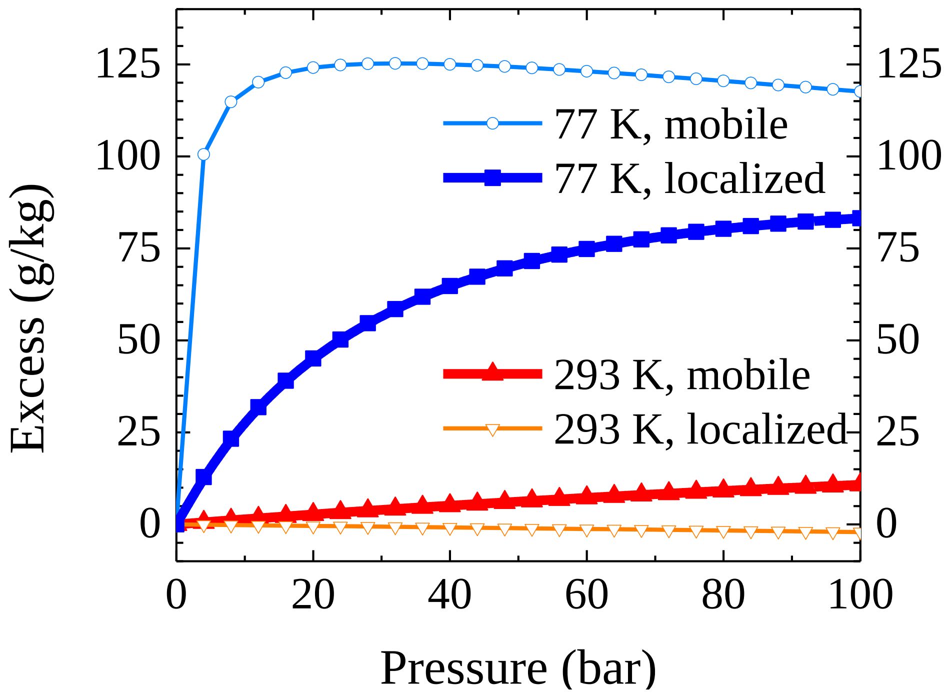


$$\chi_{Mobile}(T)=\frac{\alpha(T)\exp\left[\frac{E_B}{N_A k_B T}\right]\sqrt{\frac{h^2}{8\pi M_{Gas}(k_B T)^3}}}{\sinh\left(\frac{h\nu_z}{2k_B T}\right)}$$

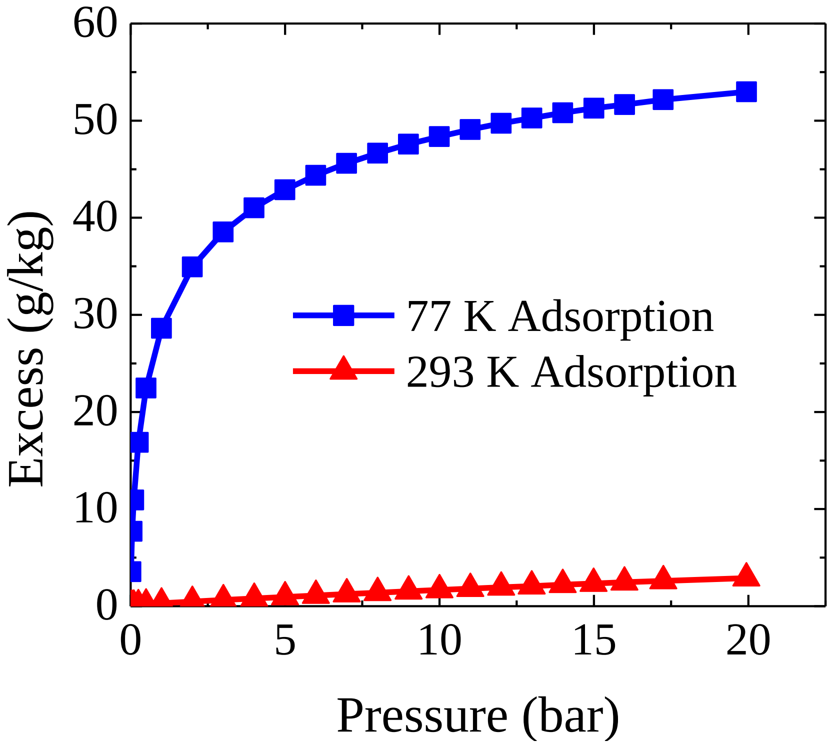
- ν_X, ν_Y, ν_Z: Vibrational frequencies
- E_B: Binding energy
- M_{Gas}: Mass of gas molecule
- N_A: Avogadro's constant
- k_B: Boltzmann's constant
- h: Planck's constant
- T: Temperature
- α: cross-sectional area per adsorption site

Localized v. Mobile

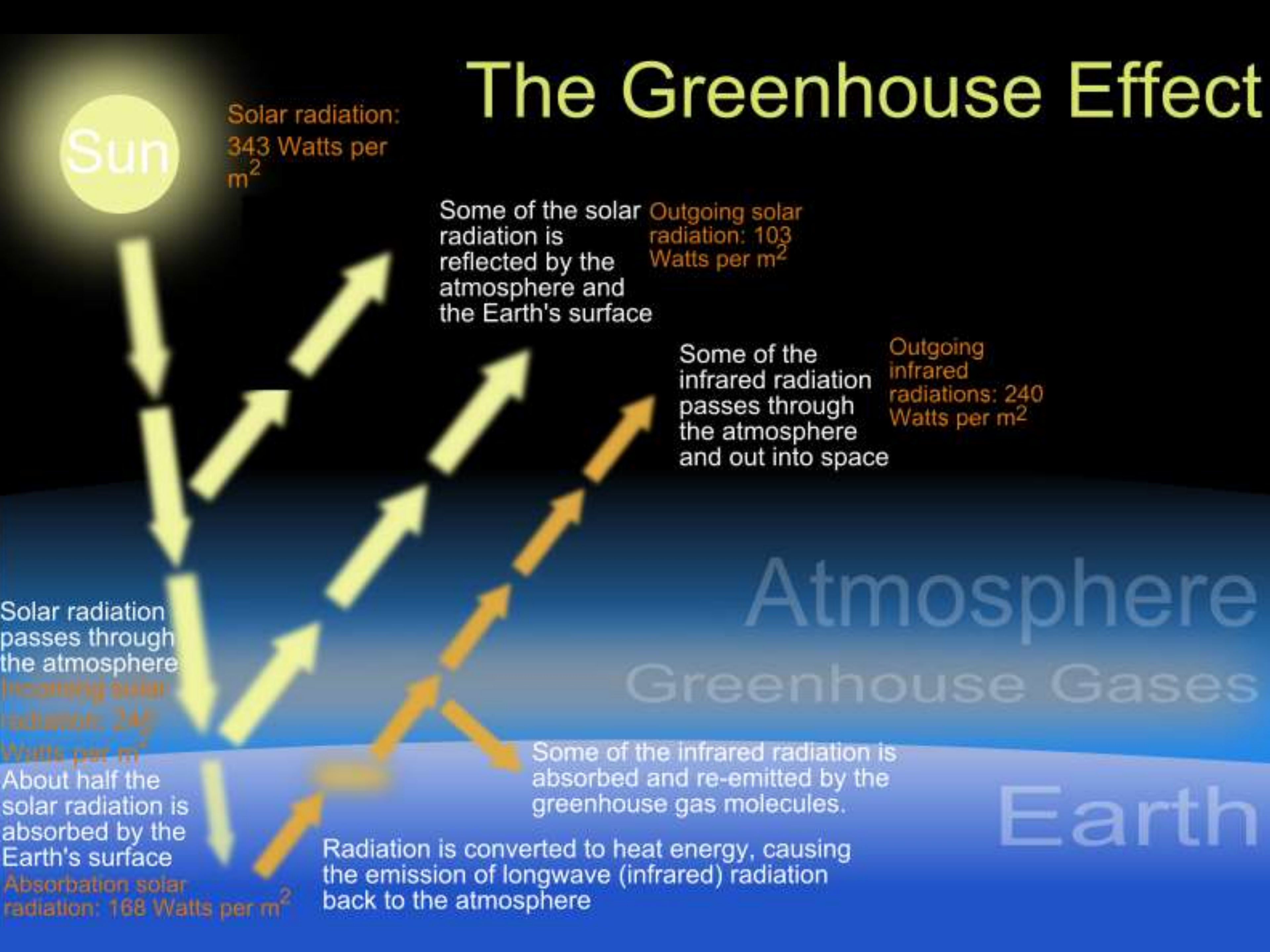
Theory



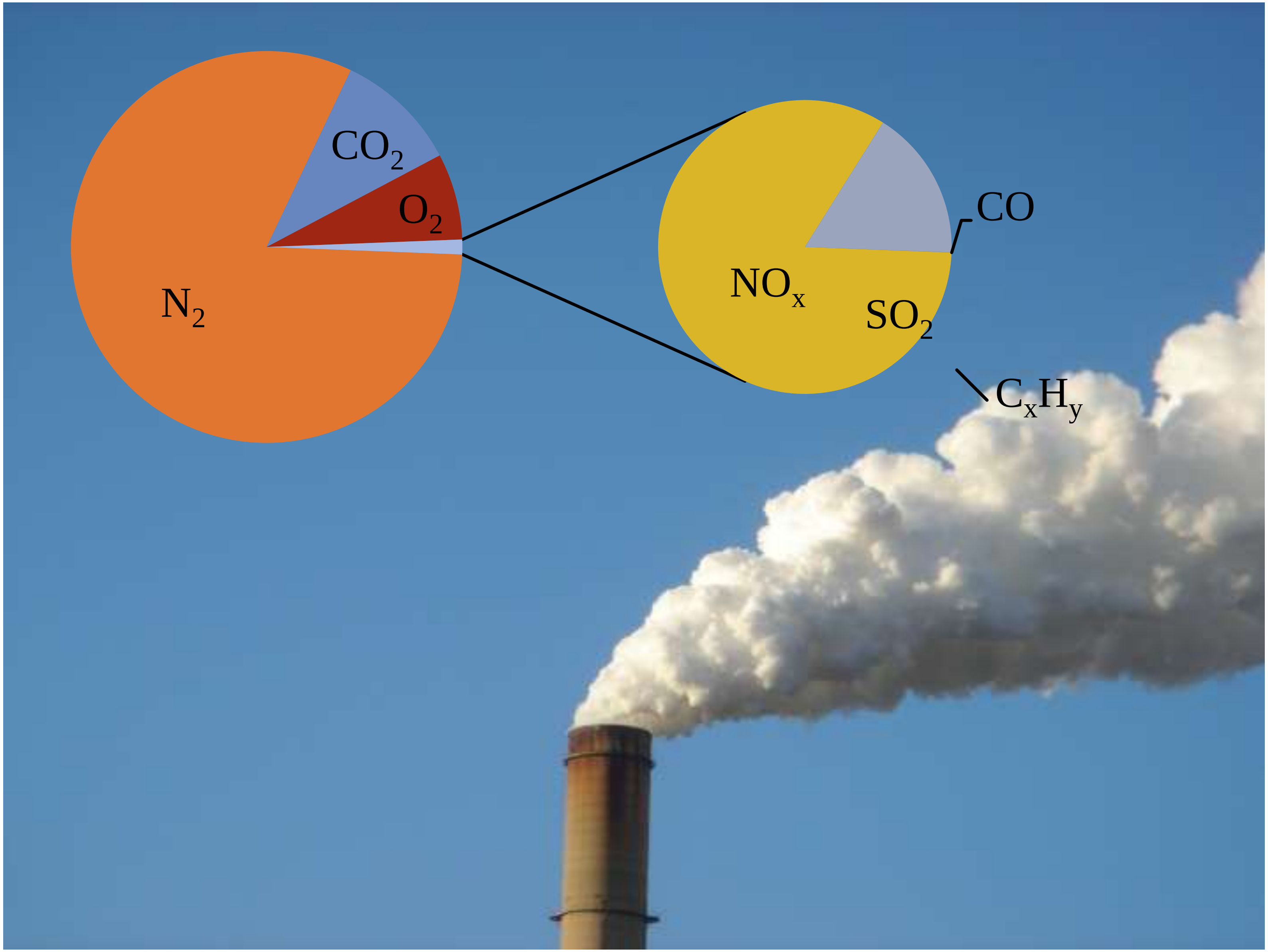
Experiment



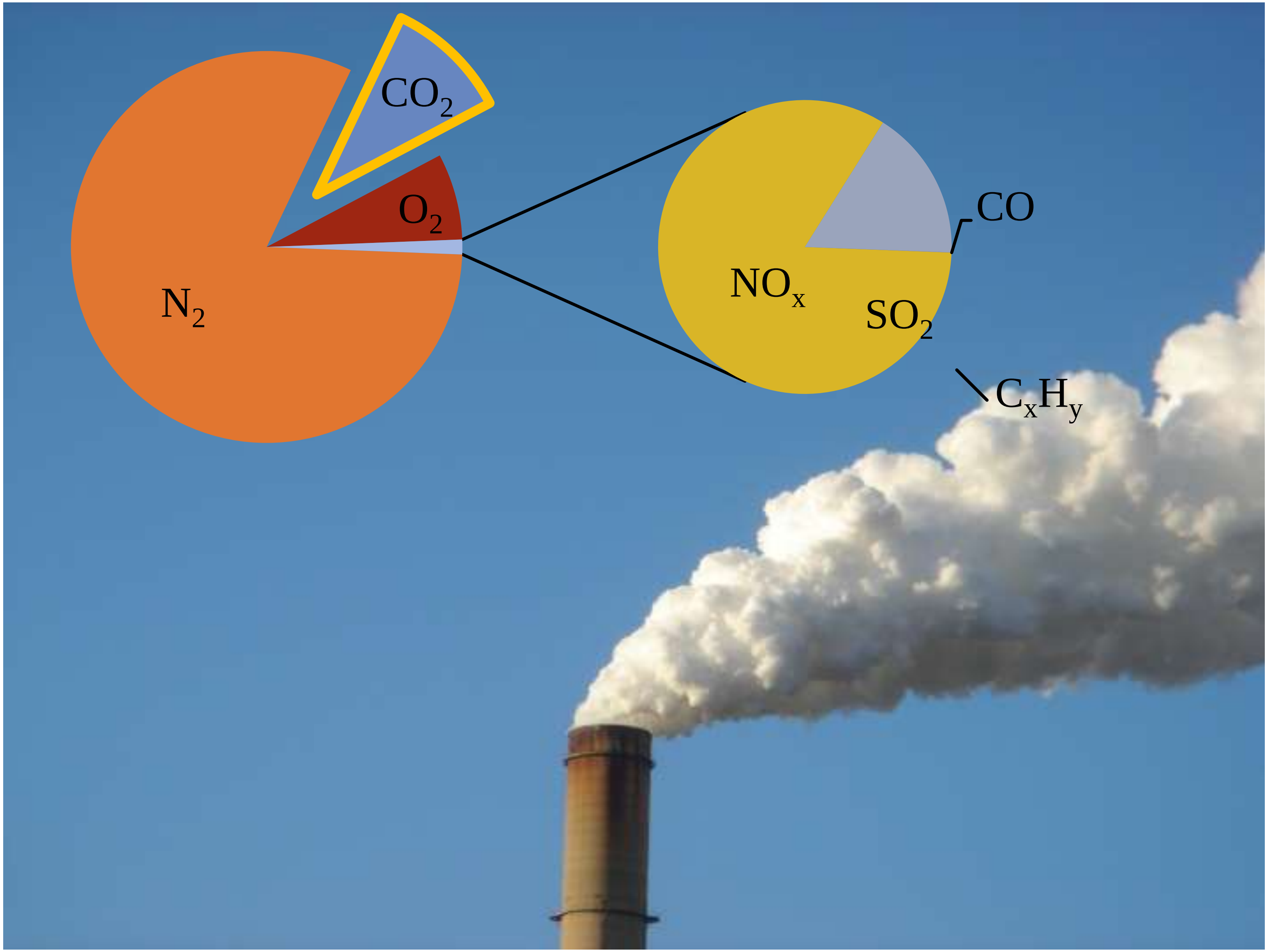
Carbon Capture


The Greenhouse Effect
Sun
Solar radiation: 343 Watts per m2
Some of the solar radiation is reflected by the atmosphere and the Earth's surface
Outgoing solar radiation: 103 Watts per m2
Some of the infrared radiation passes through the atmosphere and out into space
Outgoing infrared radiations: 240 Watts per m2
Atmosphere
Greenhouse Gases
Solar radiation passes through the atmosphere
About half the solar radiation is absorbed by the Earth's surface
Absorbation solar radiation: 168 Watts per m2
Some of the infrared radiation is absorbed and re-emitted by the greenhouse gas molecules.
Earth
Radiation is converted to heat energy, causing the emission of longwave (infrared) radiation back to the atmosphere

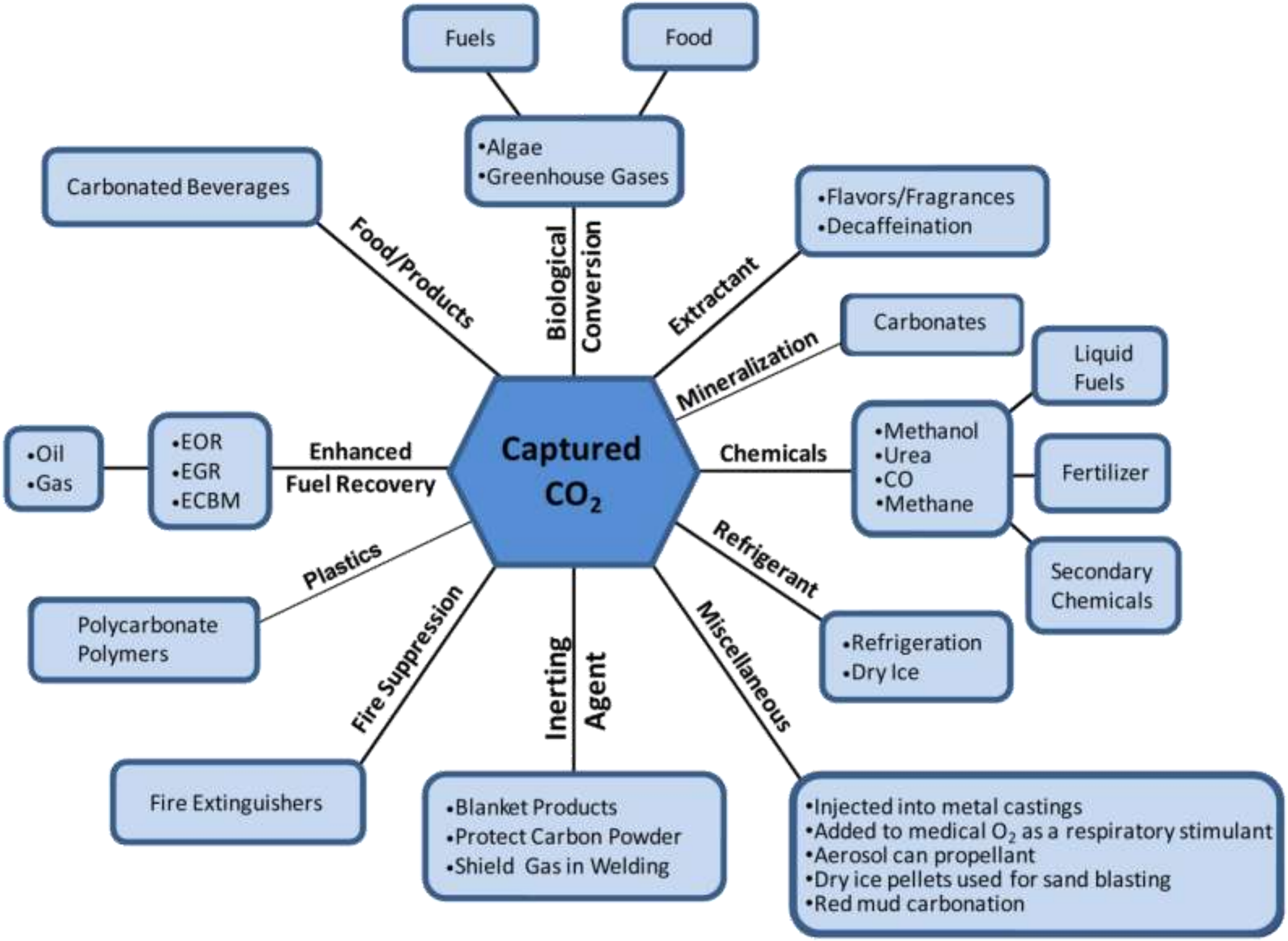
Flue Gases



Flue Gases

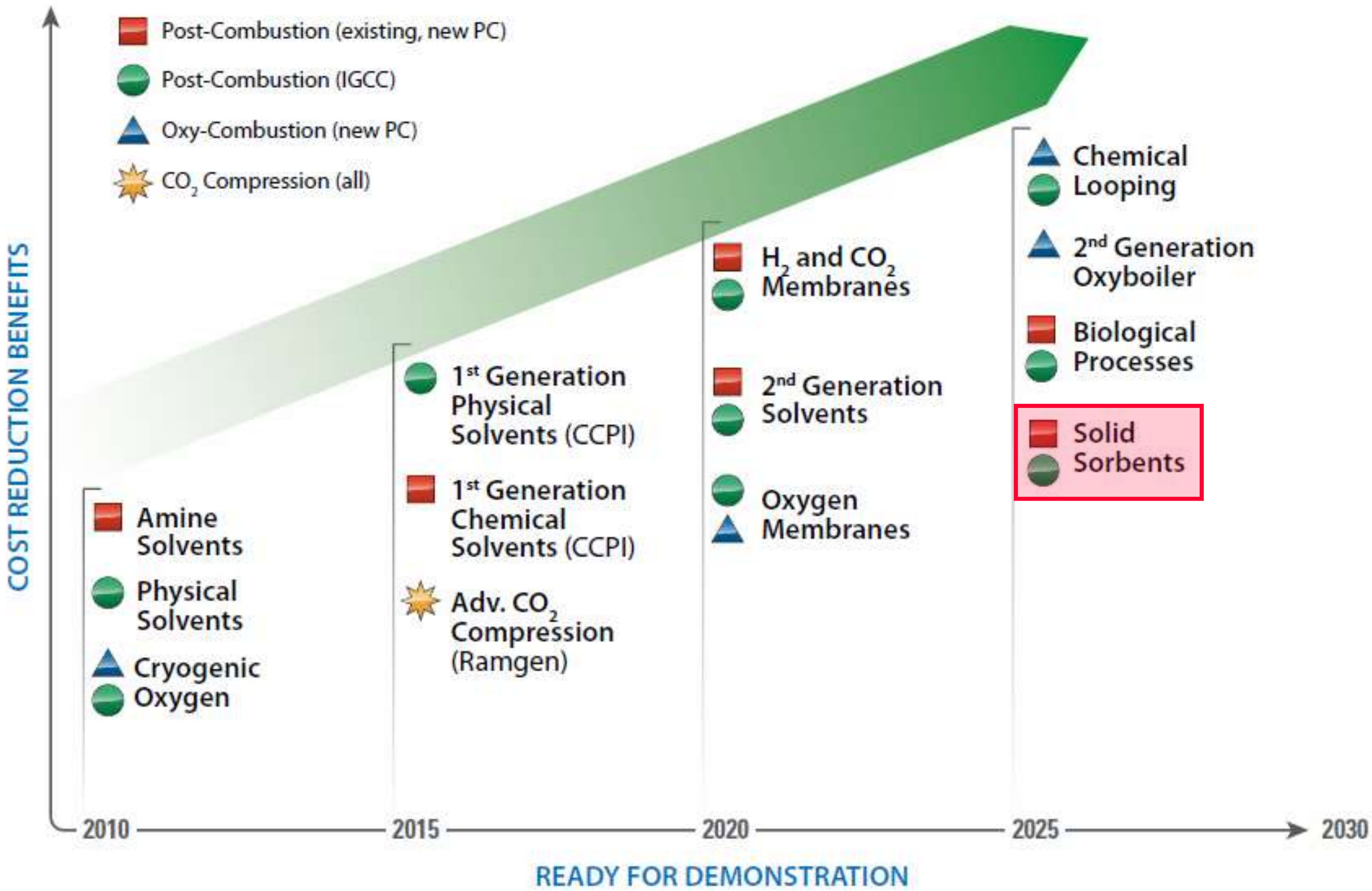


Utilization of Captured CO_2



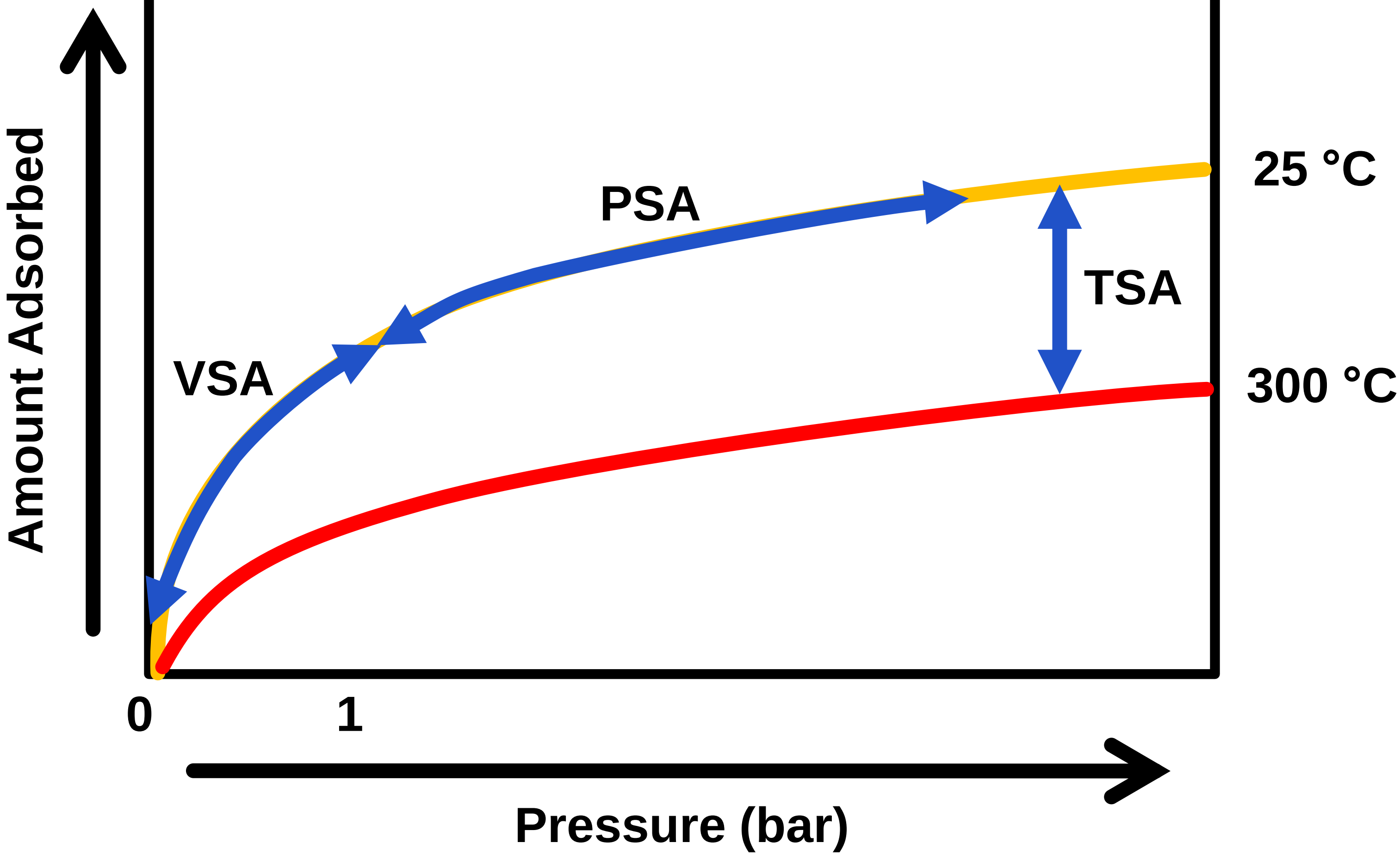
Carbon Sequestration Program: Technology Program Plan, DOE, 2011.

CO_2 Capture



DOE/NETL Carbon Dioxide Capture & Storage RD&D Roadmap, 2010.

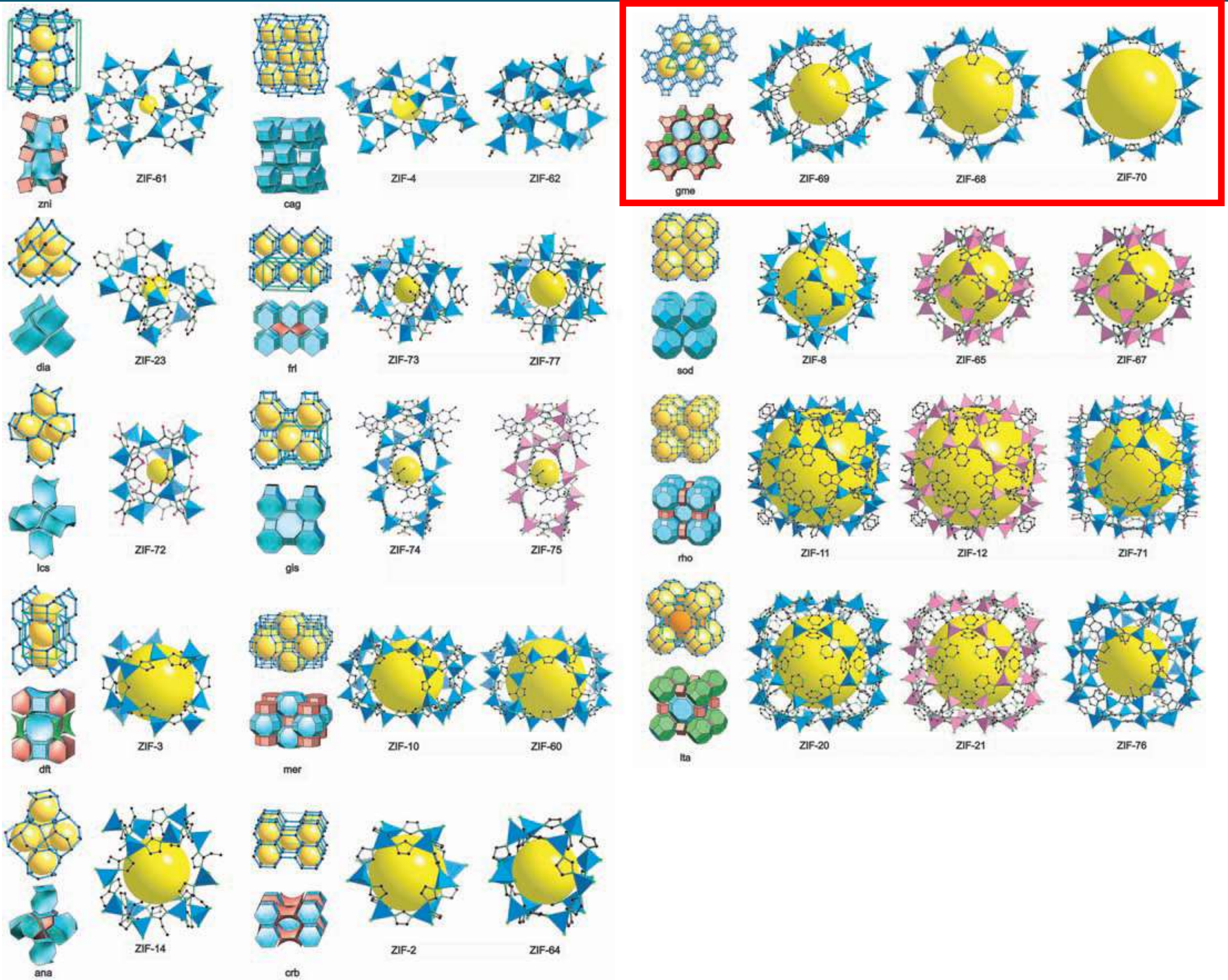
Pressure, Vacuum & Thermal Swing Adsorption



Desired Sample Characteristics

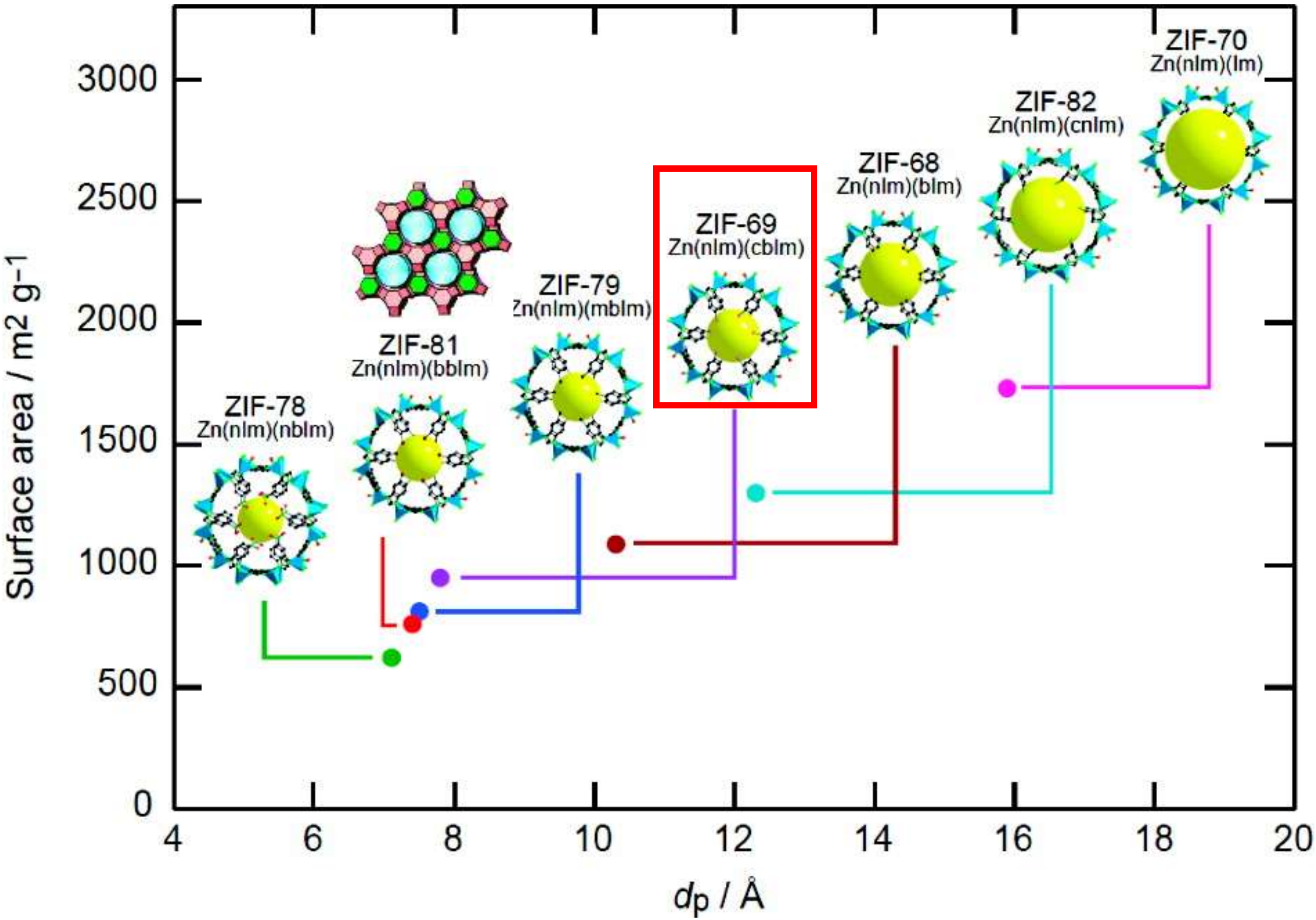
- High uptakes
- High selectivities
  - CO_2 v. N_2, O_2, CO, CH_4
- Robust
- Isotherm shape for capture process
  - Vacuum swing adsorption
  - Pressure swing adsorption
  - Temperature swing adsorption

Zeolitic Imidazolate Frameworks



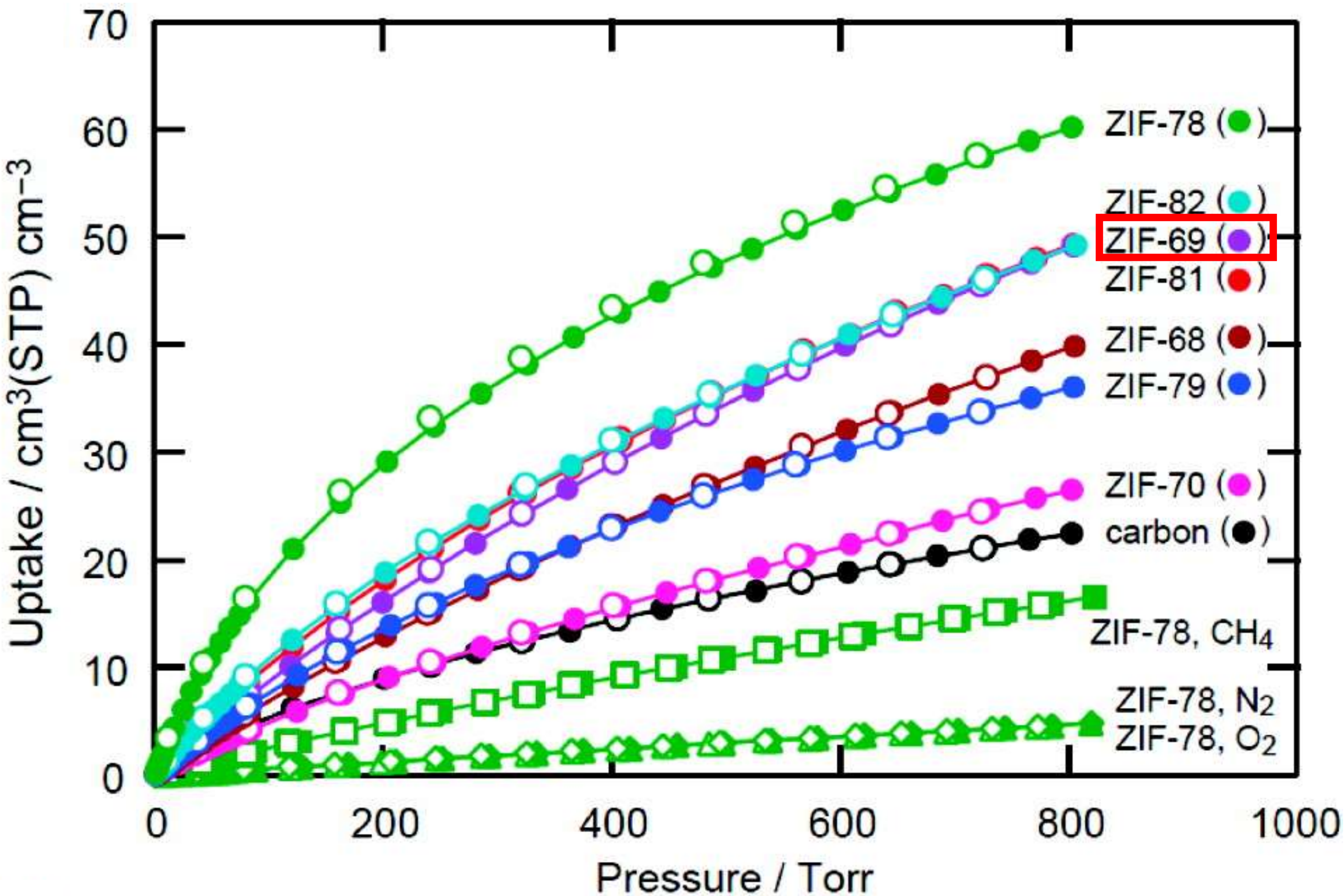
Banerjee, R., et al., *Science, 2008.* ***319(5865): p. 939-943.***

ZIFs: GME Topology



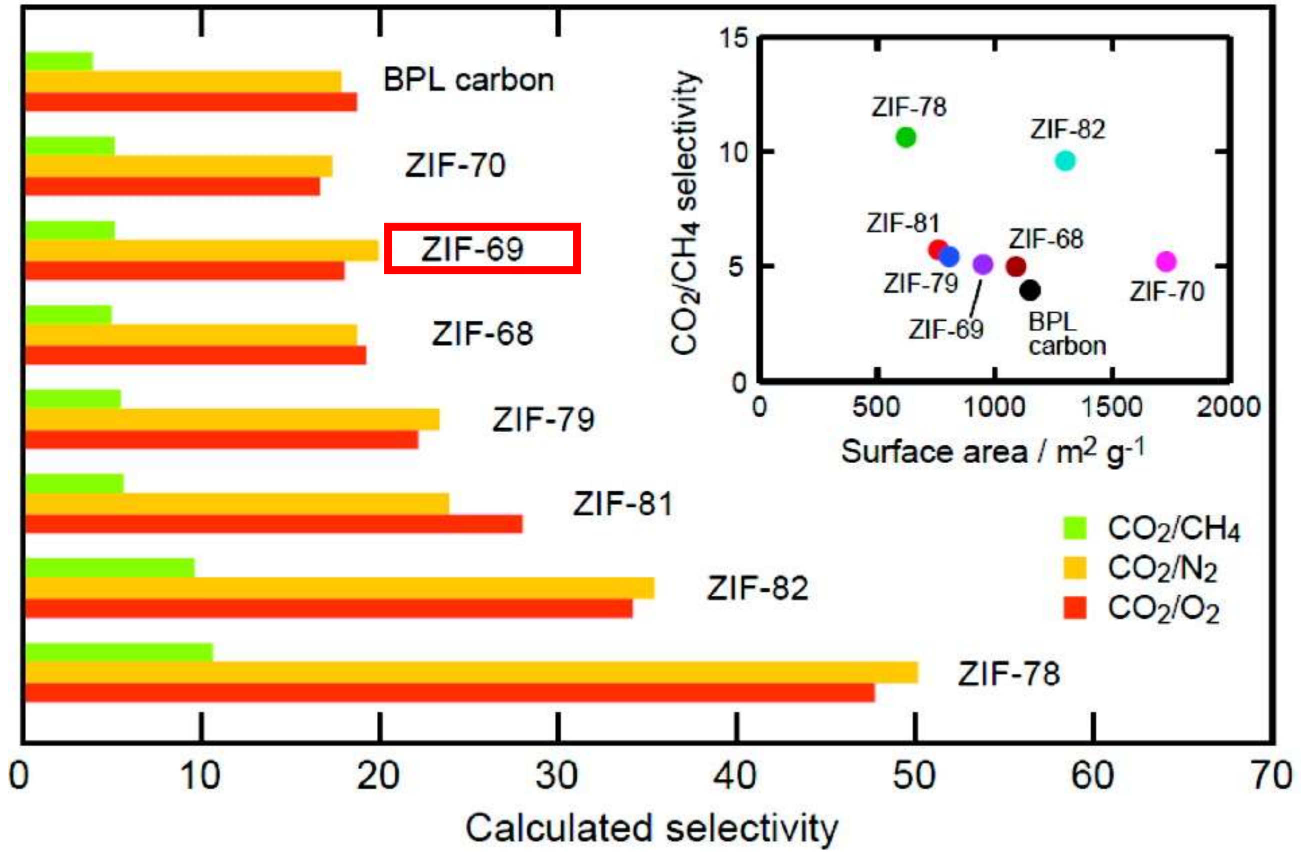
ZIFs: CO_2 Uptake

- High uptakes



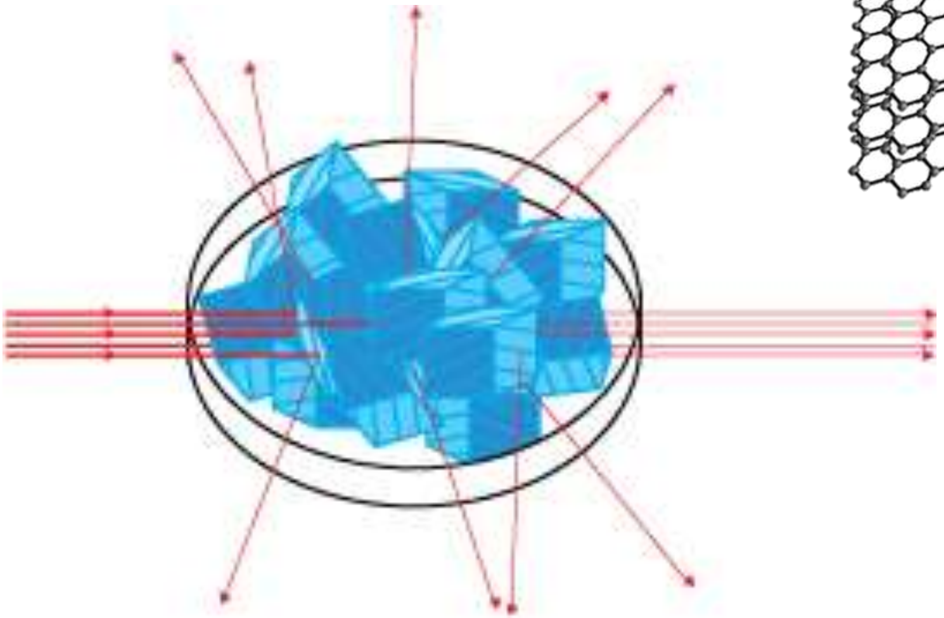
ZIFs: CO_2 Selectivity

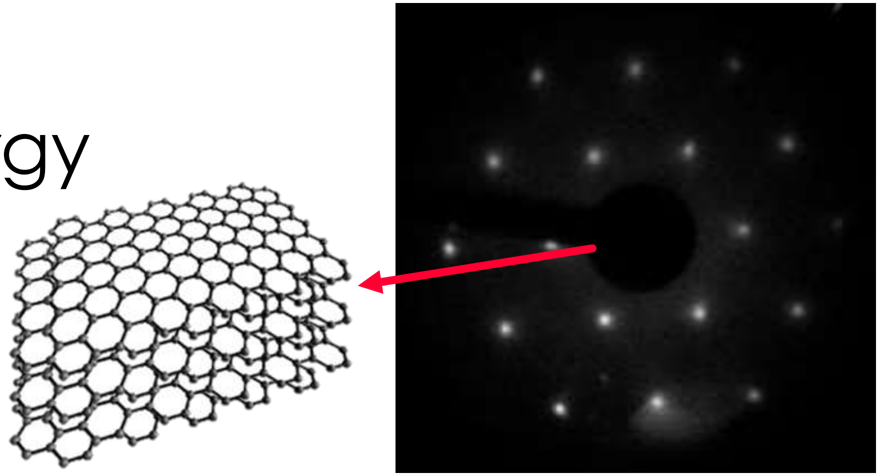
- High selectivities
  - Dipole moments

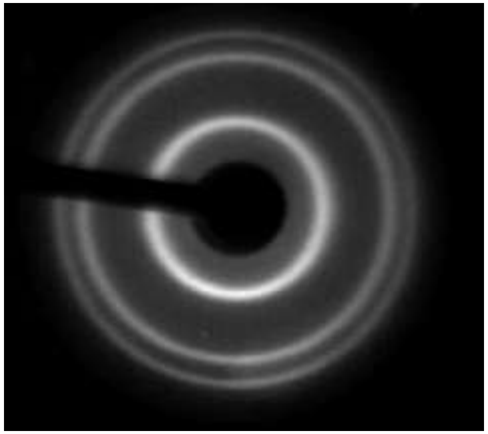


Aside: Powder Diffraction

- Elastic scattering
  - No change in energy

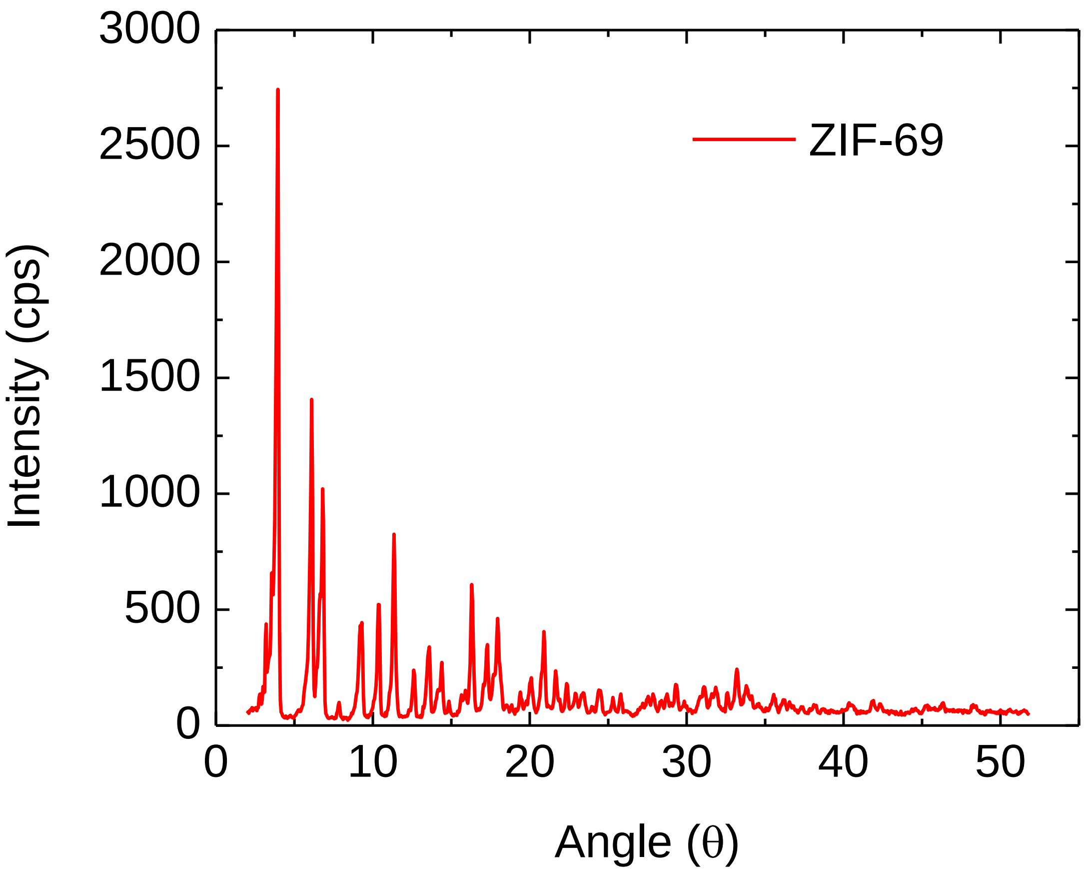


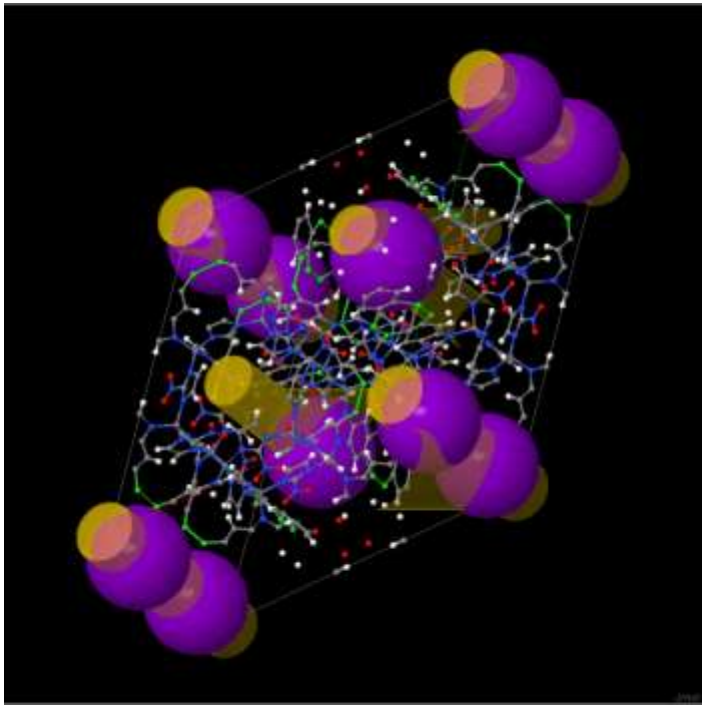




Powder Diffraction of ZIF-69

- ZIF-69 unit cell has 600 atoms
  - Compare to graphite which has 4

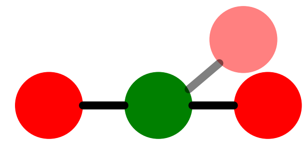


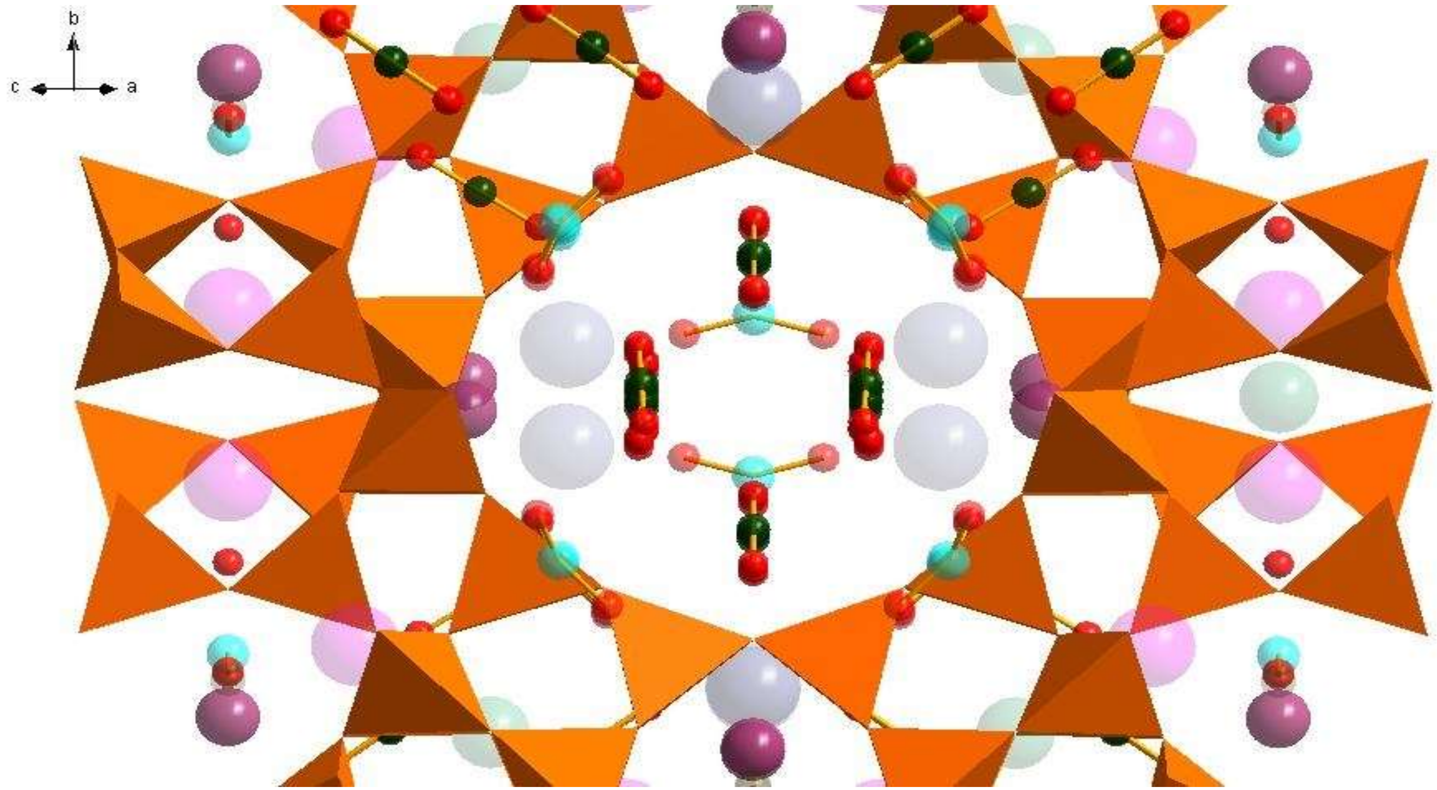


http://helios.princeton.edu/mofomics

In situ Neutron Diffraction

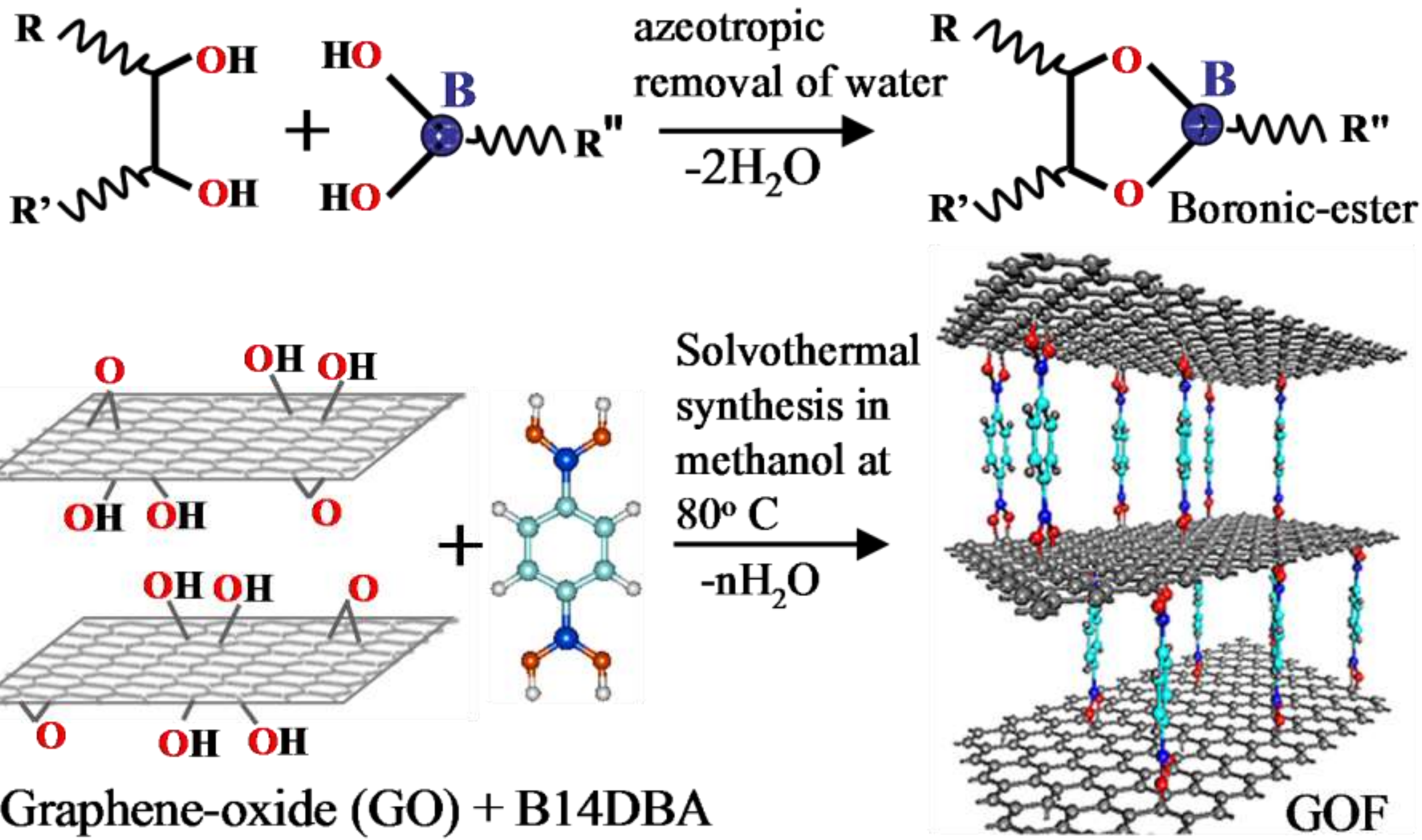
- CO_2 adsorbed in NaY Zeolite





Wong-Ng, W., Kaduk, J., Huang, Q., Espinal, L., Li, L., & Burress, J. Crystal Structure of NaY Zeolite with Adsorbed CO2 by Neutron Powder Diffraction. Microporous & Mesoporous Materials. Accepted.

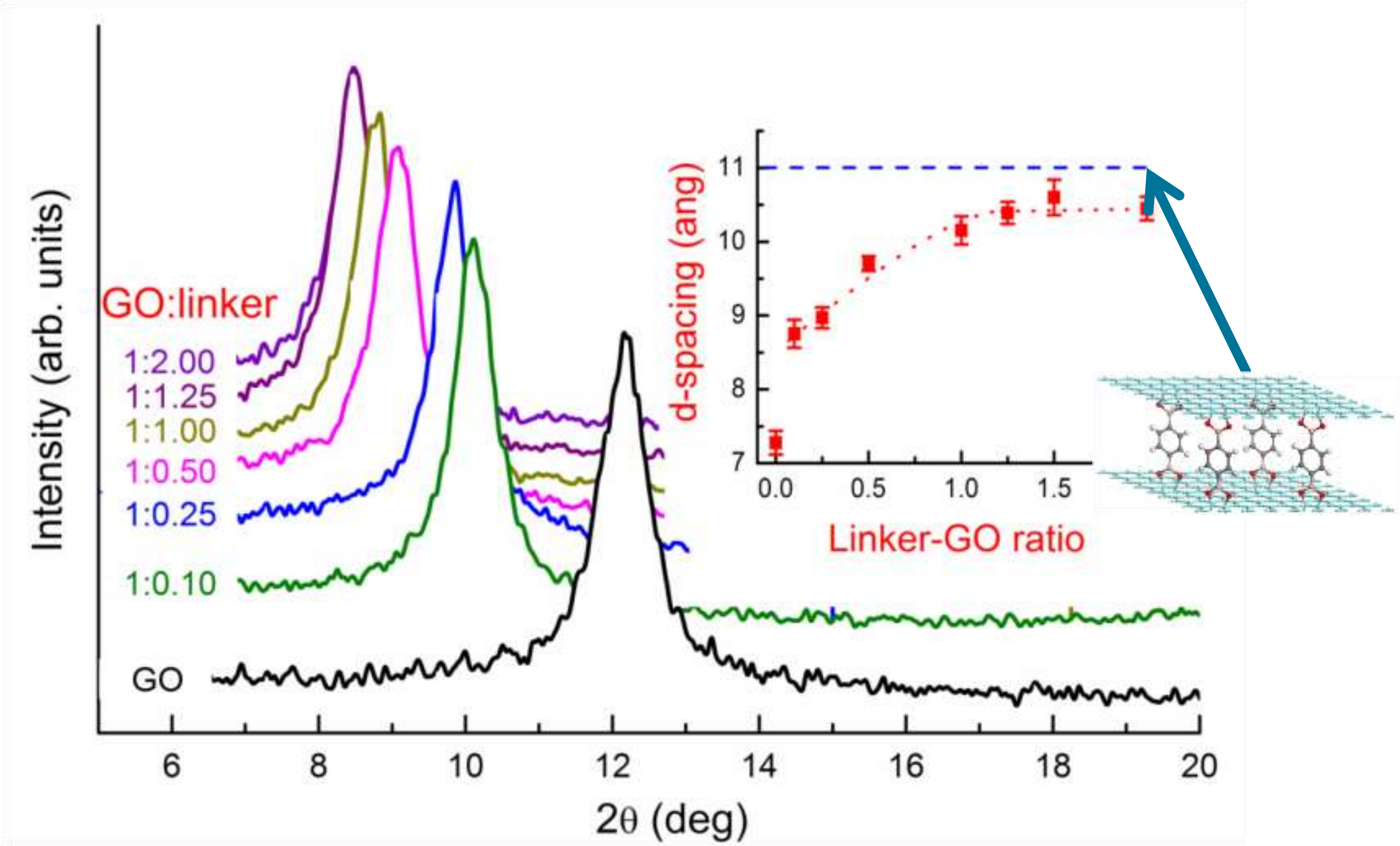
Graphene Oxide Frameworks



Graphene-oxide (GO) + B14DBA

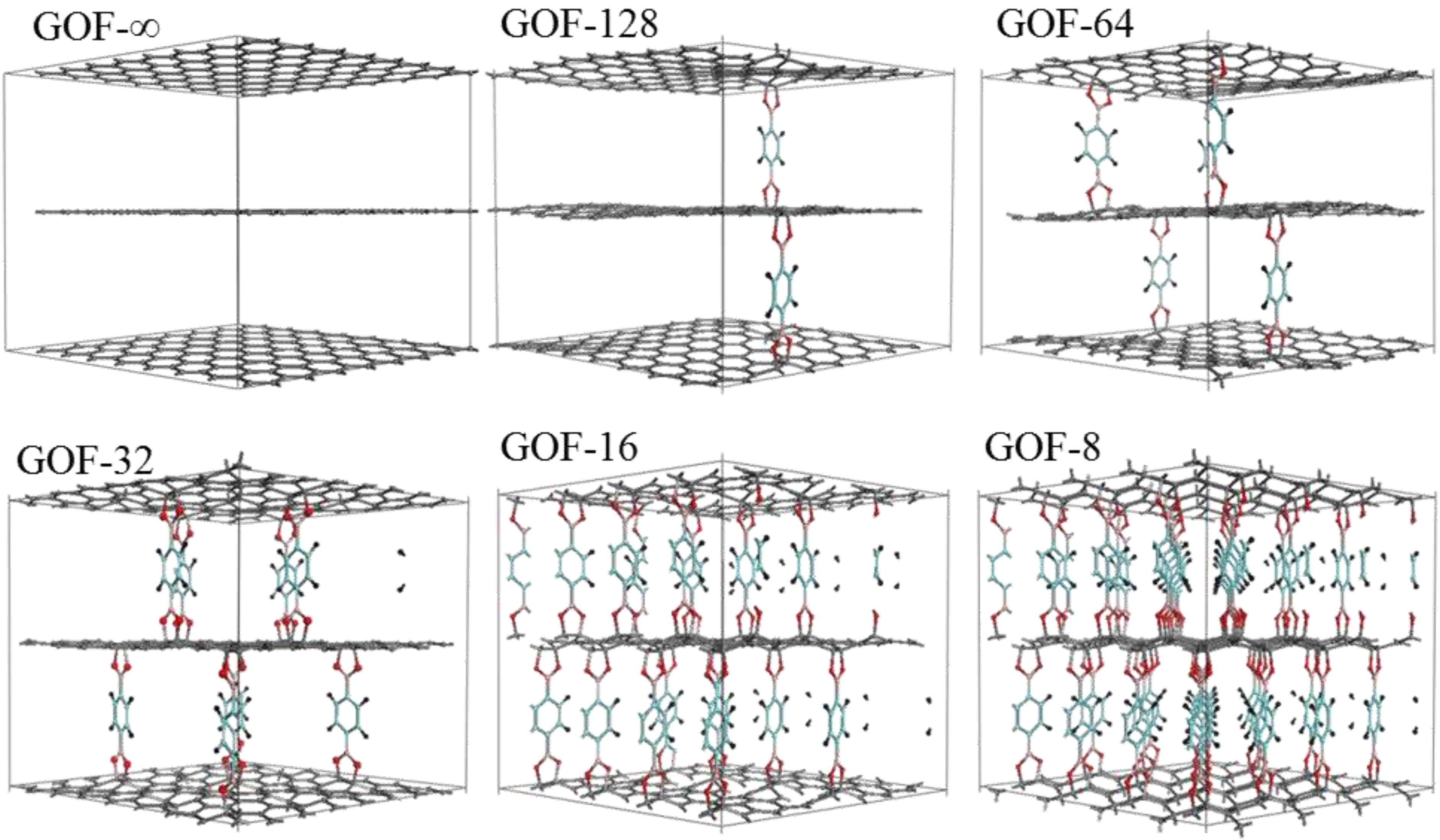
Burress, J.W., et al. *Angewandte Chemie International Edition, 2010.* ***49(47): p. 8902-8904.***

Interlayer Spacing



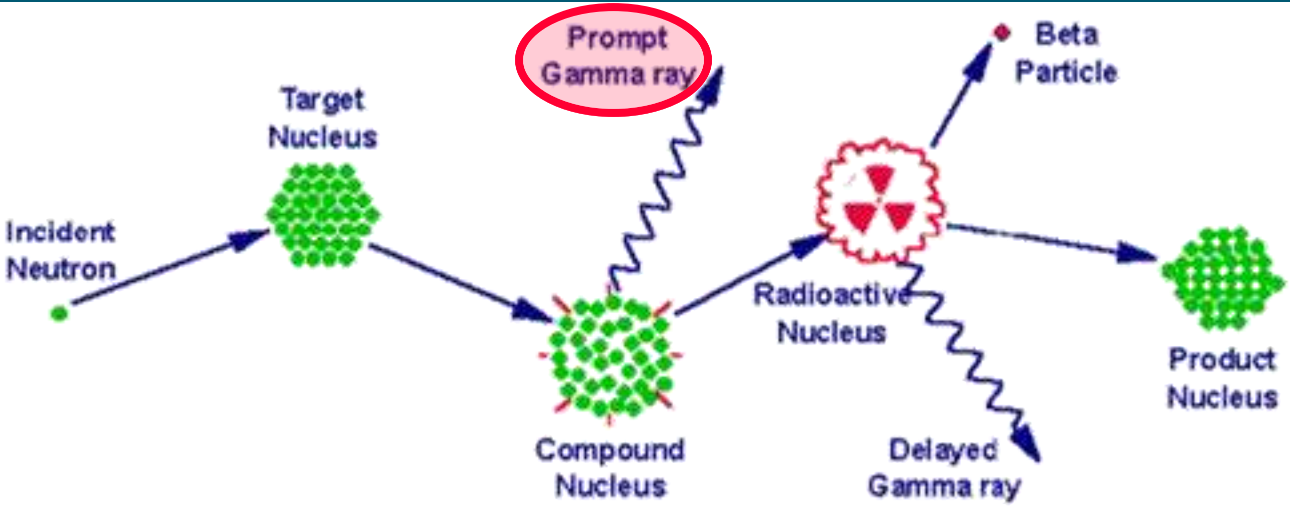
Burress, J.W., et al. *Angewandte Chemie International Edition, 2010.* ***49(47): p. 8902-8904.***

GOF Structure Optimization



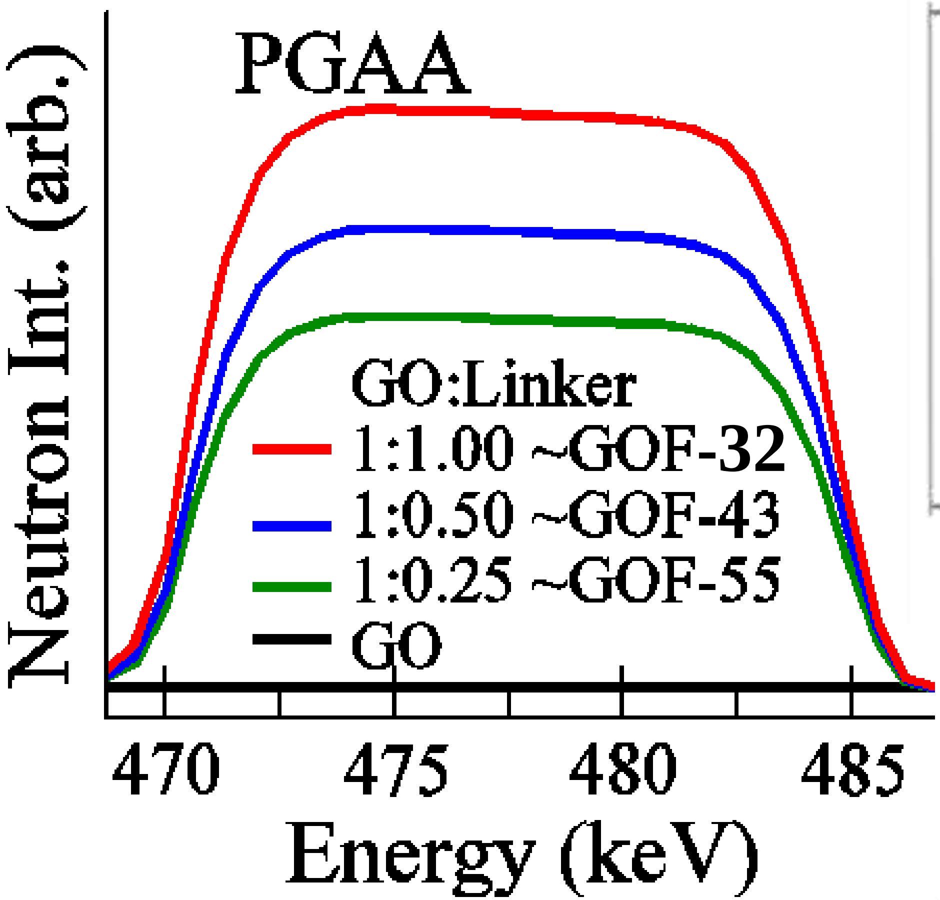
Burress, J.W., et al. *Angewandte Chemie International Edition, 2010.* ***49(47): p. 8902-8904.***

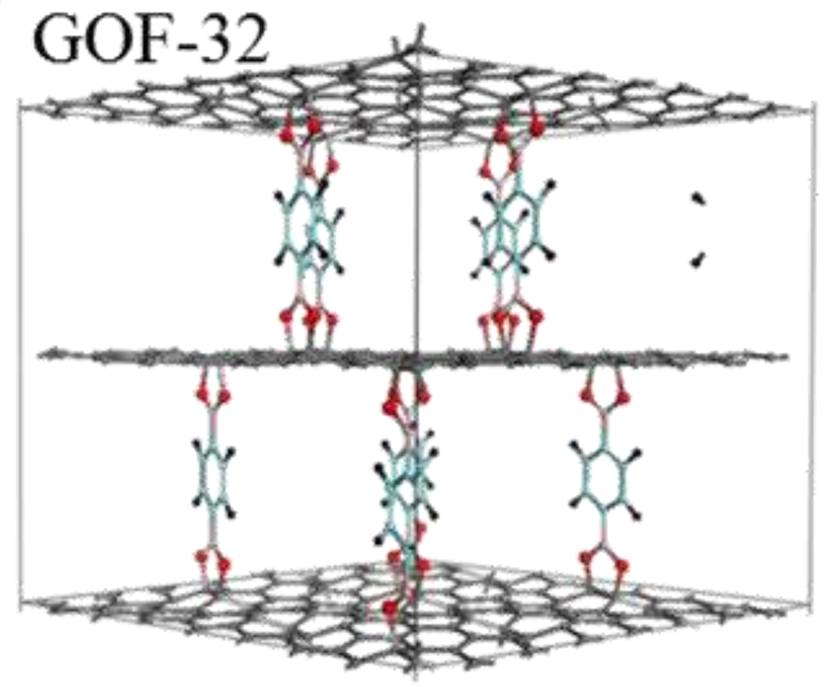
Aside: Prompt Gamma Activation Analysis



Lower detection limits for 1 gram sample	
0.01 μg – 0.1 μg	B, Cd, Sm, Gd
0.1 μg – 1 μg	Eu, Hg
1 μg – 10 μg	H, Cl, In, Nd
10 μg – 100 μg	Na, S, K, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Ge, As, Se, Br, Mo, Ag, Te, I, Au
100 μg – 1 mg	Mg, Al, Si, P, Ca, Fe, Zn, Ga, Rb, Sr, Y, Zr, Nb, Sb, Ba, La
1 mg – 10 mg	C, N, F, Sn, P

GOFs: Prompt Gamma Neutron Activation Analysis



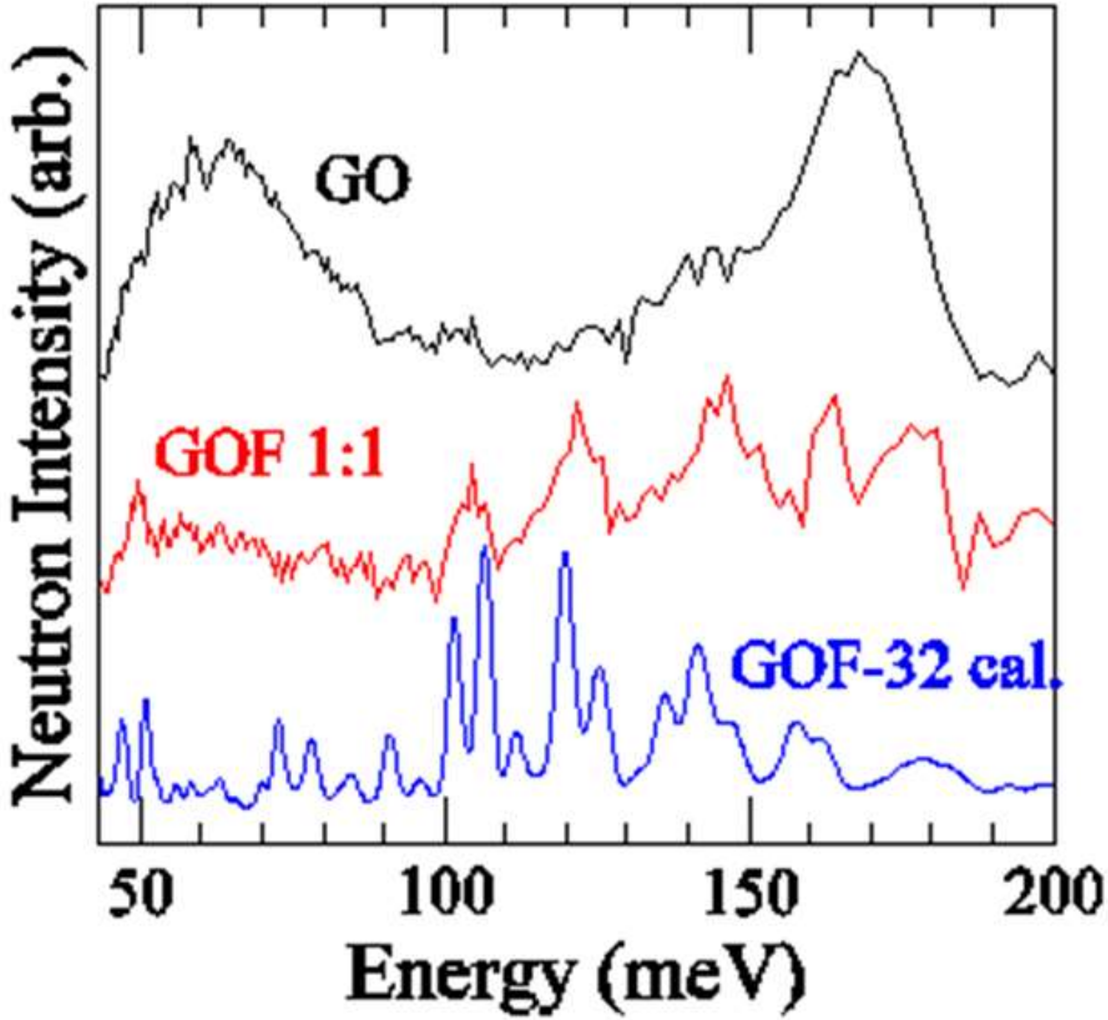


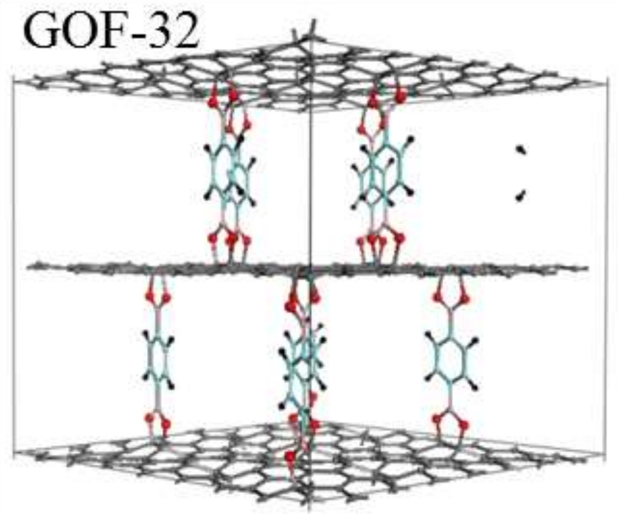
Burress, J.W., et al. *Angewandte Chemie International Edition, 2010.* ***49(47): p. 8902-8904.***

Aside: Inelastic Neutron Scattering

- Neutron experiences change in energy
- Neutrons can have energy ~ thermal energy
  - Therefore they can "see" things with ~thermal energy

GOFs: Inelastic Neutron Spectroscopy

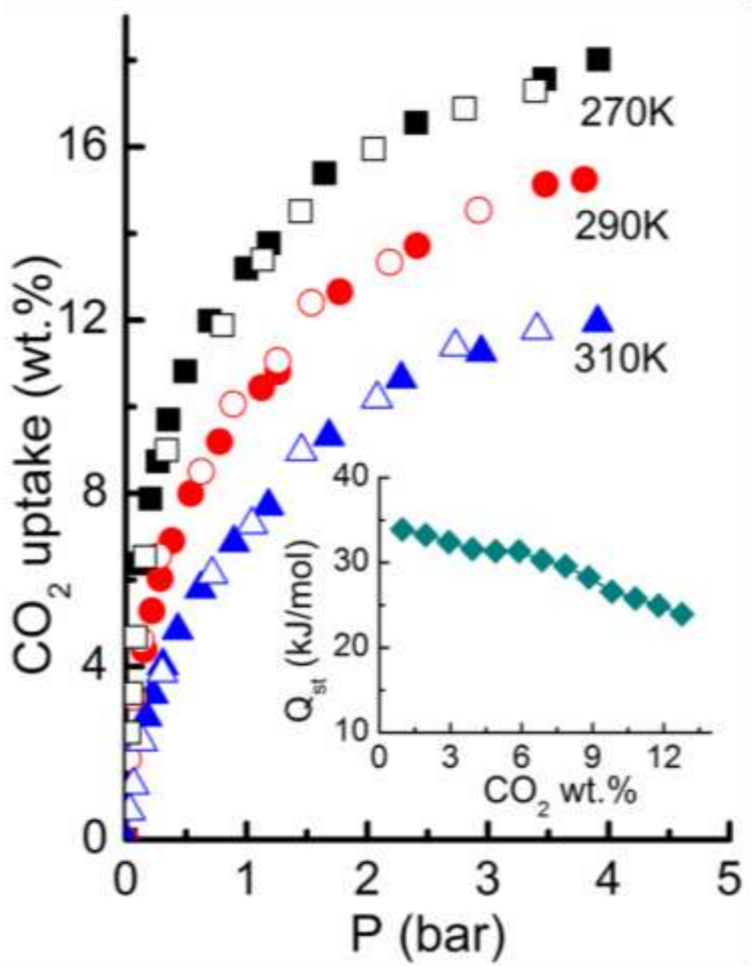




Burress, J.W., et al. *Angewandte Chemie International Edition, 2010.* ***49(47): p. 8902-8904.***

GOFs: CO_2 Uptake

- High binding energy
- Lower than expected uptake
- Increase surface area




CO2